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The Chemical Industry in 1937

THE year that is closing is one which can be regarded with satisfaction by almost every branch of industry. The chemical industry has had its fair share of the increased prosperity of British trade and, in spite of the growth of economic nationalism and unsettled world conditions, has enjoyed increased export business. A comparison of the first eleven months of this year with the corresponding period of 1936 shows an increase in the total import of raw materials valued at £66,051,000. It must be remembered that the processing of many of these raw materials and their manufacture into finished articles must have meant an increased use of chemicals, apart altogether from the many new discoveries and new developments within the home industry which have made unnecessary the importation of a growing number of raw materials. There is every indication that home products are increasingly replacing imports, and that the British chemical industry is becoming more and more self-supporting. Thus, of articles wholly or mainly manufactured, imports of chemicals, drugs, dyes and colours increased this year by only £1,224,700, as against an increased export valued at £3,653,500, compared with the first eleven months of 1936.

The export of heavy chemicals has improved considerably, that of bleaching powder rising from 529,387 cwt. to 721,080 cwt., sodium carbonate—including soda crystals, soda ash, and bicarbonate—from 3,599,309 cwt. to 469,090 cwt., and caustic soda from 1,817,622 cwt. to 2,471,850 cwt. in the first eleven months of 1937. Imports of these chemicals are negligible by comparison. Again, production of sulphuric acid (the traditional index of chemical trade) in Great Britain and Ireland during the first half of the year, in terms of 100 per cent. acid, was 402,700 tons manufactured by the chamber process and 161,700 tons by the contact process—a total increase of 34,300 over the corresponding period of 1936.

Another significant trend is the increasing number of chemicals and intermediate products now manufactured by the home industry. Thus, between January and September of this year there were no imports at all of refined ammonium carbonate, acetylene tetrabromide, sodium salicylate, sodium sulphide, refined calcium phosphates and sulphate, and titanium oxide, many of which formerly enjoyed a fair import market in Great Britain.

It should be mentioned that the progress of the dyestuffs industry has been well maintained, as shown by the import and export figures. Imports of finished dyes and coal tar decreased in value by £87,404 between January and November of this year, as compared with the corresponding period of 1936. Dyestuffs exports rose by over £137,605 in the same period. Cresylic acid exports increased by 345,369 gal., and tar and creosote oils by over 7,000,000 gal. in the January/November period of 1937, as compared with the same period last year.

Despite serious disturbing factors, such as the wars in Spain and China, the fertiliser market this year showed a gratifying increase of export business. Over 91,000 tons more sulphate of ammonia was exported in the first eleven months of 1937, than in the same period last year. Mention should also be made of the great stimulus given to the consumption of lime and basic slag by the Government's undertaking this year to reduce the cost of these to the farmer by 50 per cent. and 25 per cent. respectively, for the limited period of three years. Moreover, new fertiliser factories have come into existence this year, including one for the manufacture of sulphate of ammonia from waste ammonia, and another for the conversion of household refuse into a humus-like fertiliser. Many old lime kilns and lime works have been started up again, and many years' accumulation of waste calcium carbonate from sugar beet factories has begun to find a market. This year has also seen the formation of a new private company to undertake the fixation of atmospheric nitrogen for the manufacture of nitrogenous fertilisers.

A feature of industrial activity during the year has been investigations directed towards national self-sufficiency. On account of the international situation, any investigations of this nature arouse a

The Chemical Age wishes all its Readers, Contributors and Advertisers a Happy Christmas and Prosperous New Year.

great deal of public interest which may be out of all proportion to the progress actually made. A case in point is the production of oil from coal. According to an estimate circulated in the House by the Secretary of Mines in July, nearly 41,000,000 tons of coal would be processed by one or other method of oil production in 1937, or only about one million more than in 1936.

The production of motor spirit by the processes of hydrogenation, high temperature carbonisation and low temperature carbonisation would be, it was estimated, 37.5, 53.5, and 1.0 million gal. respectively in 1937, as against 33.3, 51.2, and 0.8 in 1936; a total increase of 6.8 million gal. In addition to this, respectively 91 and 6 million gal. of heavy oils would be produced in 1937 by high and low temperature carbonisation methods respectively, a total increase of 4.4 million gal. over 1936. This improvement seems small compared with the import of 1,135 million gal. of motor spirit between January and October, 1937—an increase of 64,000,000 gal. over the previous year.

These figures show how greatly home oil production will have to be expanded if we are to be in a position in any way approaching that of independence of foreign supplies. This would be a formidable task, and as Lord McGowan pointed out in the House of Lords, " this is a matter for Government consideration and Government action. It is for the Government to decide whether the national safety demands a certain production of oil from coal in this country." The Government set up the Falmouth Committee to inquire into the whole position. Whatever findings of the committee are eventually adopted, and whatever process is finally considered to be the most advantageous, it is quite certain that the Government will have to be prepared to set aside a very large sum of money if the problem is to be tackled wholeheartedly. Satisfactory reports were issued during the year as a result of tests carried out for the Government on two low temperature carbonisation plants, one situated in Durham, and the other in Kent. Further, the foundation stone was recently laid of a new carbonising plant in South Wales to be capable of dealing with 500-700 tons of coal per day. There will also be a coal oil distillation plant for the production of aviation spirit, fuel oils, etc. Private and semi-private enterprise is, therefore, by no means inactive. The Fischer-Tropsch process has received additional support from abroad by the announcement of the erection of a Fischer-Tropsch plant in South Africa, the first plant of this nature to be erected in the Empire. Five plants are already operating in Germany, and both France and Japan are erecting works to operate this process.

Up to November 30 last, this country imported nearly 1,200,000 cwt. of calcium carbide, as compared with just over one million cwt. for the corresponding period last year, and 997,000 cwt. for the first eleven months of 1935. Thus, it is an event of importance that we are now to have, for the first time, a calcium carbide manufacturing industry in this country. After considering a number of schemes for the manufacture of calcium carbide and allied products, a Government Committee, set up by Sir Thomas Inskip, Minister for the Co-ordination of Defence, recommended a scheme submitted by the British Oxygen Co. The scheme, which is being proceeded with, entails the erection of two factories, one in South Wales, and the other in Scotland. It is interesting to see that both the new coal carbonisation plant and a calcium carbide factory are to be erected in one of the Special Areas. During the year, the areas have begun to be regarded by the manufacturer, not so much as objects worthy of support from the humanitarian point of view only, but as advantageous business propositions deserving of the closest consideration. Spreading of this correct view was undoubtedly assisted by a lecture on the subject delivered before a meeting of the Institution of Chemical Engineers.

Turning now to an annual event which gives an indication of the developments being made in the industry, namely, the British Industries Fair, there were a number of especially interesting products at this year's exhibition. Among the high-lights were potassium permanganate, manufactured for the first time in this country, crystallised soda, made by a new process, and commercially-produced oxalic acid. Other interesting exhibits were a series of strontium salts, camphor prepared on the commercial scale, and two new ranges of dyestuffs for leather and for direct dyeing of acetate artificial silk respectively. A proportion of important papers read during the last twelve months before meetings of the chemical bodies and those described in technical journals are referred to in this issue, but three symposia call for special mention. The first dealt with plastics in times of national emergency and was held by the Institute of the Plastics Industry towards the end of January. The object of the symposium was to place on record an account of the present position of the plastics industry, the uses to which plastic materials are put, figures of production and use, and to emphasise the national importance of the plastics industry in times of emergency. Special attention was given in the papers read at the symposium to the supplies of raw materials. Possible sources at home were discussed for those materials which are normally imported. More than two hundred papers were presented at a congress held in London by the International Association for Testing Materials. It was a most valuable addition to our knowledge of the subject contributed by specialists from different parts of the world. Another specialised symposium was arranged by the International Society of Leather Trades' Chemists on the scientific and technical aspects of wetting and detergency in February.

What of the prospects for 1938? Every sign by which the condition of trade can be judged points to the continuance of the present satisfactory state at an even higher level during the coming year. There are some who talk with gloom of trade cycles and confidently assert that they can already discern the figure of " slump " on the industrial horizon. As we have already pointed out, in many cases these pessimistic views are attributable to political agitation of a particularly vicious nature. Further, there are those who put down the present industrial prosperity as due, to a great extent, to the rearmament programme. The effect on industry in general of the increased Governmental expenditure on armaments has been grossly exaggerated; it has brought business to comparatively few trades. In any case, as officially stated recently, expenditure in accordance with the programme has not yet reached its peak. No, we must accept the message the tested signs give us and the opinions of those in high authority who are in a position to draw unbiased conclusions from the evidence before them.

A Message from Lord Leverhulme

Lord Leverhulme, President of the Society of Chemical Industry.

WHEN I was honoured with an invitation to fill the presidency of the Society of Chemical Industry for a second year, I had not counted on the pleasant opportunity it would give me of renewing for 1938 the good wishes I addressed to your readers for the year now coming to a close. It may be profitable to examine how far our anticipations have been borne out.

First place I think must be given to the work of the Chemical Council, which has certainly exceeded the promise associated with its first year's work. Its influence on the business side of the publications belonging to contributory bodies has been appreciable in spite of the heavy increase in the cost of paper and printing generally. It has made a very promising start in securing financial assistance for scientific publications both from individuals and from corporate bodies. The effect of this help will be more noticeable in the coming year than in 1937. In addition, substantial progress has been made in building up a fund for other forms of expenditure to a degree that entitles one to look forward, possibly some years ahead, to the fulfilment of the long cherished idea of what one might call a "temple of chemical science," a home for the chemical societies of this country consistent with the position they hold in the world's estimation.

The Society's publications in their new form have had a year's trial and have given great satisfaction. It may be some time before the weekly journal settles down quite to the form we have looked forward to, but matters are moving in that direction, and I hope if my successor has the opportunity of wishing you well in 1939, he will be able to report that our aim has been realised.

Our annual meeting was made more notable than usual by the happy inspiration of holding it in Harrogate, rather than in one of the industrial centres, and by the outstanding success of the Yorkshire committee in the quality of the programme provided and the manner in which it was carried out. Those who have attended many of these annual gatherings say it is one of the happiest meetings within their memory.

We are looking forward in 1938 with the greatest possible pleasure to holding the annual meeting in Canada during June. Our Canadian sections are entering with zest on the task of exceeding even the efforts of their predecessors in 1921 and in 1928.

The improvement in industry to which I referred last year has been maintained, and with it the increased support of the Society by members of the chemical profession and industry. I hope 1938 will see us further on the road towards restoring the ground lost during the depression of the previous few years. On behalf of the Society I wish your journal and its readers every success and happiness during the coming year. position they hold in the world's estimaton.

Some Technical Advances in the Heavy Chemical Industry

By
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THE heavy chemical industry, like other branches of chemical manufacture, has no cause to be disappointed with the past year. The internal trade has been well maintained, but there is no doubt that a more stable international political situation would assist the flow of international trade. Price changes generally in industry during the year have been upward, and this is true of chemical plant due to the increases in the price of iron and steel and to some extent in labour.

Sulphuric acid production is usually a good index of prosperity for it is used in so many processes and industries, and here again it is gratifying to observe that the official figures for the first six months of the year show continued increase. The acid made in 1935 was 936,000 tons, in 1936 it was 1,043,000 tons and in the first six months 564,000 tons, which was at the rate of 1,128,000 tons for the year. The proportion of acid made by the contact process again shows a slight increase, this (according to one authority) being 40 per cent. of the total for the first six months of 1937 as compared with 39.2 per cent. for the equivalent period of 1936. Supplies of spent oxide for acid making are dependent upon the activity of the gas industry, and although this industry has again to record a gratifying increase in gas production, it has not been enough to keep pace with the growing demand for sulphur. No doubt the Spanish situation will have affected the supplies of pyrites. Whatever the cause, the fact remains that brimstone is making headway as the raw material for acid manufacture, and this year it has been used for just over one-fifth of the sulphuric acid made.

The price of sulphuric acid has been stable for a considerable time, and any advance is relatively more serious than for most chemicals, since it affects so many processes and products. The rise in acid prices that has occurred has been due: (1) to the rise in freights—pyrites freights are now 13s. to 16s. a ton in place of the standard basis rate of 8s.; (2) to the rise in the raw materials; and (3) to increased labour charges. Thus adverse external conditions have overtaken increased internal efficiency and technical improvements.

An acid plant has been erected in which the source of sulphur is the saturator gas from the sulphate of ammonia plant, except at such times when the ammonia plant is idle when a sulphur burner is brought into use. This plant consists of two Glover towers, one Gaillard-Parrish tower chamber, in which the chamber acid is atomised, one half-packed tower, in which the chamber acid is circulated, and three Gay-Lussacs followed by a water-mash tower. The plant produces the equivalent of 80 tons of 30 per cent. acid per week at an efficiency of 95 per cent., and it is ultimately intended to use the waste heat in the burner gases to concentrate the acid to 95 per cent. strength. In view of the

need for home production of as much raw material as possible, it seems curious that the Thylox process which extracts sulphur from coal gas has not been brought into operation for dealing with coke oven gas, and particularly for dealing with gas used in the steel industry. Many plants of very large capacity are operating in Germany, U.S.A. and Japan.

Production of the Air-SO_2 Mixture

Several patents have been taken out during the year for the production of the air-SO_2 mixture needed for manufacture. The use of finely-divided pyrites is a feature of some of these. For example, C. F. Silsby (U.S.P. 2,028,416) allows finely-powdered pyrites to fall down a roasting chamber at 930-960° C. up which ascends a current of hot air sufficient to burn the sulphur and leave the required excess of oxygen, the burnt material being removed continuously by a conveyor at the base of the chamber. H. O. C. Ingraham (U.S.P.2,030,021) projects a cloud of fine sulphide ore down a chamber in which a current of air is also passing downward; the cinder is removed from the bottom while the hot gases pass upwards through an annular space surrounding the shaft to provide the heat for the roasting. Other patents visualise burning melted sulphur, as for example, I. Bencowitz (U.S.P. 2,031,403) who sprays molten sulphur into a heated combustion chamber where it meets a whirling current of hot air. To complete combustion the resulting mixture is then passed through chequer brick-work. As a second example, D. Teatini (B.P.461,665) superimposes a sulphur-melting chamber on at least two combustion chambers, the sulphur being run to these combustion chambers separately or in series. Air is introduced into the centre of the apparatus and the SO_2 is removed at the side.

Russian investigators suggest that no less than 90 per cent. of the lead used in the construction of the plant for the lead chamber process can be replaced by cast iron and certain acid-resistant minerals. Investigation has also been carried out in Russia on the speeding-up of the tower process. L. I. Markov (*J. Chem. Ind. Russ,* 1937, *14,* 190-192) claims to have shown that oxidation of nitric oxide and sulphur dioxide takes place only in the liquid phase, so that the optimum conditions of sulphuric acid manufacture would be secured by retaining oxides of nitrogen in the acid and by working at temperatures less than those usually considered suitable for the tower process. Other workers have shown that the reaction $NO+O \rightarrow NO_2$ is completed in the Gay-Lussav tower, thereby increasing the absorption capacity of the plant. Usiukin and Sutschkov have shown that the velocity of reaction between nitric oxide and oxygen and that of the absorption of NO_2 by aqueous sulphur dioxide is much greater at 0° C. than at 30° C., and claim that considerable economies can be effected by conducting the tower process at the former temperature. The corrosion of lead by sulphuric acid has been shown to be a maximum in 77 per cent. acid; in weaker acid it increases more with rising content of nitrosylsulphuric acid than in more concentrated acid, and in all instances rising temperature accelerates corrosion.

Removal of Arsenic

Arsenic in the burner gases can be removed according to Adadurov, Tzeitlin and Fomitscheva (*J. Appl. Chem. Russ. 10,* 807) by passing the gas at 350° C. over a copper oxide-manganese dioxide catalyst containing 5 per cent. of beryllium oxide. When the catalyst has picked up 0.1 per cent. of As_2O_3 it begins to lose its activity, but may be regenerated by extraction with 15 per cent. caustic potash, from which the arsenic can be recovered by precipitation with lime. The growing tendency to remove sulphur dioxide from power station gases will lead to a valuable additional source of sulphur when means can be found for utilising the weak solutions recovered. An account (again from Russia) is published of experiments in which the sulphur from coal containing between 2.9 and 4.6 per cent. sulphur was oxidised in presence of manganese sulphoxide or manganese chloride whereby acid of a strength of 18 to 20 per cent. was obtained; 70 per cent. acid was obtained by oxidation of the SO_2 in a high-tension field. It is also suggested that pyrites derived from coal could be used for 60 per cent. acid production.

Work on the contact process appears to be principally concerned with vanadium as a catalyst for the reaction. The activity of the catalyst is dependent both upon the nature of the base and of the vanadic acid, probably being effected by the conversion of one type of vanadic acid to another. Molybdovanadates appear to be excellent catalysts. The great advantage of the vanadium catalyst for acid manufacture lies in its immunity to arsenic poisoning. Olsen and Maisner (*Ind. Eng. Chem., 29,* 254) have investigated this claim by preparing four catalysts and comparing their service while subliming weighed quantities of As_2O_3 in the preheater of the converter. The most efficient catalyst, containing 6.6 per cent. V_2O_5 without promoter on an inert carrier with potash added, had an efficiency greater than 99 per cent. When treated with 12 per cent. of As_2O_3 its efficiency only fell to 95 per cent. The other catalysts, which contained barium as promoter, also showed similar steady deterioration under arsenic treatment, so that the immunity claimed is regarded as only relative. It is emphasised that unless the arsenic is introduced with the gas, experimental results cannot be relied upon. Siegert (*Angew. Chem., 60,* 319) also notes the steady accumulation of arsenic in the vanadium catalyst, and states that the $V_2O_4-V_2O_5$ equilibrium on which the catalytic action depends is thereby displaced. He also accepts the implication of a steady poisoning and states that it is greatest with catalysts low in alkali and is decreased by raising the temperature. Potassium and silver vanadates as catalysts are converted into sulphates with simultaneous increase in the activity of the catalyst. It has been held that the vanadium catalyst is poisoned by carbon monoxide, but this is probably due to the reducing action of CO on SO_2 and can be decreased by raising the temperature of the catalyst.

Preparation of Concentrated Nitric Acid

Most of the publications dealing with nitric acid have been concerned with the problem of manufacturing concentrated acid. One proposal involves distillation of the dilute nitric acid with phosphoric acid, in which the amount of phosphoric acid added is 0.5 to 1-0 gram-mol. per gram-mol. of water. U.S.P.2,027,578 involves absorption of oxides of nitrogen under pressure. E.I. Du Pont de Nemours and Co. in B.P.456,446 cool the gases from ammonia oxidation to remove water, compress to liquify N_2O_4, and pass the gases into the upper part of a tower down which flows dilute nitric acid to produce 60 per cent. acid in the middle, the N_2O_4 being there introduced at a temperature of 50 – 80° C. and under a pressure of 20 atmospheres a little above inlets through which warm compressed air is blown into the tower. The colour variations found in nitric acid during production are ascribed by Adadurov and Konvisor (*Ukrain. Chem. J., 12,* 221) to the presence of varying amounts of blue N_2O_3 and yellow NO_2. Considerable amounts of nitric oxide may be present in the liquid phase and thus lead to absorption of oxygen from the gas. Under atmospheric pressure the absorption of NO, and consequently of oxygen, rises with falling temperature, but the velocity of oxidation increases with temperature. To reconcile these divergent conditions the authors recommend the maintenance of a temperature of 20 to 22° C. in the lower part of the absorption tower, with cooling in the upper portion.

The concentration of orthophosphoric acid has been discussed by Burrows Moore and T. H. Barton (*J.C.S.I. 56,* 273). It is interesting to note that the pipe still principle that is being employed in tar distillation and has been for some time in use in the petroleum industry is used for phosphoric acid concentration. At increasing temperatures such as are met with as the acid becomes more concentrated under the action of heat, orthophosphoric acid decomposes into other forms; it is completely changed into pyrophosphoric acid by about 260° C., this change commencing at about 160° C., and metaphosphoric acid begins to be formed at

290° C. Suitable concentrating apparatus giving a short time of contact enables high temperatures to be used without molecular change and under these conditions a suitable temperature has been found to be 100-213° C. Hot phosphoric acid attacks all otherwise suitable constructional metals and alloys, but fused silica is almost unaffected even at temperatures as high as 300° C., and is considered by the authors to be the only constructional material suitable for the concentration of acid of high chemical purity. The authors describe a new form of tower concentrator constructed of fused silica and suitable for the concentration of sulphuric acid, the purer forms of phosphoric acid and other liquors capable of being concentrated by evaporative methods without the deposition of salts. In this apparatus gaseous fuels, preferably those which, like coal gas, are free from sulphur and arsenic, are burnt inside the tower in contact with the solution to be concentrated, the hot products of combustion passing in counter-current to the descending liquor, which is subdivided into very thin streams or droplets. The production of phosphoric acid of 50 to 60 per cent. strength without the need for concentration is the object of an I.G. Farbenindustrie patent (B.P.470,428.. Sulphuric acid of preferably 70 per cent. strength is used at a temperature between 80 and 100° C. for the initial decomposition of the phosphate rock, the amount added being more than double that corresponding stoichiometrically to the lime content of the rock. The precipitated gypsum is filtered off and washed with a little water. The filtrate, which contains phosphoric acid and sulphuric acid is treated with more crude phosphate and the freshly precipitated gypsum is again filtered. This alternate treatment and filtration is continued as long as sulphuric acid remains in the liquor, a temperature of 80° C. being maintained throughout the operations. It is claimed that decomposition is effected to a far-reaching extent and within a very short time, with no more than a 10 per cent. excess of sulphuric acid. The fluorine escapes to a much greater extent than with the usual processes, but is not recovered. Reference should also be made to the paper by Dr. Lehrecke reproduced in THE CHEMICAL AGE, October 30, 1937, p.347.

Liquid Ammonia Process for Soda Ash

The question has been asked whether the Solvay process for soda ash is threatened with a new competitor in the liquid ammonia process. It is understood that this system is under development in Russia, and Germany, and, most significant of all, that a Japanese plant has been put into operation that is making 50 tons of soda ash a day. The use of ammonia enables the intermediate carbamates to be produced readily, and if necessary isolated owing to their insolubility in liquid ammonia if salts such as NaCl and NH_4Cl are absent. The reaction as a whole is given by the equation :

$$2NaCl + CO_2 + 2NH_3 + H_2O = Na_2CO_3 + 2NH_4Cl \quad (1)$$

The stages in which the reaction occurs are given by the four equations :

$$2NH_3 + CO_2 = NH_4CO_2NH_2 \quad \ldots \quad \ldots \quad (2)$$

$$NH_4CO_2NH_2 + NaCl = NaCO_2NH_2 + NH_4Cl \quad (3)$$

$$NaCO_2NH_2 + H_2O = NaHCO_3 + NH_3 \quad \ldots \quad (4)$$

$$2NaHCO_3 = Na_2CO_3 + H_2O \quad \ldots \quad (5)$$

Controlling Conditions

Since the thermal effect of sodium carbonate formation is very small, it is inferred that the action is independent of temperature and time, provided that the amount of salt used corresponds to its solubility at a given temperature. The process can therefore be conducted at atmospheric temperatures. The impurities commonly present in salt are insoluble in liquid ammonia and no special initial purification of the salt is needed. It is said that the yield of ammonium carbonate according to equation (2) is 100 per cent.; this reaction is carried out at 0° C. to avoid corrosion troubles, the constructional metals used being tin, steel and chromium (as plating). The sodium carbonate is filtered and washed with liquid ammonia before proceeding to reaction (4) in which it is steamed at 300° C., the washing being necessary to remove chloride since reactions (4) and (5) would otherwise be reversible. It is claimed that the soda ash is of 99 per cent. purity and that the ammonia is recovered as chloride of 93 to 95 per cent. purity, the remainder being salt. The Russian process also starts by preparing ammonium carbamate. Sodium chloride is independently dissolved in liquid ammonia, the surplus ammonia being evaporated. The two solutions are mixed and react according to equation (3), after which the sodium carbamate is filtered off, washed with liquid ammonia and steamed as in the Japanese process.

Little appears to have been published during the year on alkalies other than ammonia, but three patents dealing with the concentration or purification of caustic soda seem to merit mention. A method has been used in the past of determining the moisture content of coal by distilling the wet coal with a mixture of hydrocarbons such as benzole and toluole with which water is not miscible. It has been left to the inventor of B.P. 469,352 to apply this simple process to the dehydration of caustic soda. The process is claimed to be applicable to many substances which formerly required a high temperature for dehydration, such as the caustic alkalies, zinc chloride, magnesium chloride and sulphate, etc. To carry out this partial pressure distillation method, the use of kerosene or some equivalent hydrocarbon boiling between 150 and 300° C. is suggested, the apparatus employed being the standard still, arranged for removal of the residual product. Four advantages have been claimed for this process : (1) with iron and steel equipment corrosion is reduced to 10 per cent. or even to 5 per cent. of that usual with the normal high temperatures, (2) when dehydrating caustic soda, for example, costs are reduced by 50 per cent., and (3) the air in the manufacturing plant is not contaminated with caustic soda or salt.

Electrolytic Production of Caustic Soda

When caustic soda is produced electrolytically, it usually contains chlorates and metallic impurities such as iron. The I. G. Farbenindustrie (B.P. 468,637) has developed a process for the electrolytic purification of caustic soda from these bodies. Electrolysis of the solution using iron anodes converts the chlorates into chlorides; electrolysis of the hydroxide solution using other anodes, e.g., nickel or graphite leads to deposition of the metallic impurities. In practice, electrode nets composed of iron and nickel are immersed in the caustic solution at 100° C., and using the iron as the anode, a current having a density of 10 amps. per square metre of electrode surface is passed, and the chlorate is converted into chloride. The current is then reversed and is increased in density to 30 to 40 amps. per square m. of electrode surface, when the metallic impurities, iron and copper are deposited on the iron electrode. The same firm (B.P. 472,754) has improved its " heptahydrate " process for removing salt from caustic soda, in order to obtain a still purer product. The original process treated a lye containing 50 per cent. of NaOH in water with 2 parts of salt per 100 parts of soda by diluting to 38 per cent. caustic, cooling to 14° C., while stirring, the cooling being continued until the pulp was just sufficiently fluid to pass through pipes. The crystals of heptahydrate, $2NaOH, 7H_2O$, were centrifuged off, and the mother liquor again cooled to deposit a further 20 or 25 per cent. of caustic soda. The crystals when melted contained 0.6 per cent. of NaCl. It was found that more intensive centrifuging failed to make any improvement, nor was it found that the mother liquor associated with the crystals could be displaced by washing with water at 5° C., i.e., lower than the m.p. of the heptahydrate. It has now been found that by washing with slightly less water than the mother liquor to be displaced at a temperature maintained between the narrow limits of 10 and 14° C., a finished product can be obtained of 38 per cent. strength and containing only 0.1 to 0.2 parts of NaCl per 100 parts of NaOH.

Space does not permit detailed reference to the many researches that have been made upon the production and utilisation of salts. It is noted that electrolytic methods

appear to be gaining favour, and attention may be called to an interesting paper on the electrochemical manufacture of permanganate by R. Desmet (*L'Industrie Chim. Belge*, May, 1937) which described the formation of manganate by heating an MnO_2-KOH mixture which is subsequently ground in a current of air or oxygen at 500° C., and is then electrolysed to permanganate, the conditions necessary being that the manganate formed must be protected from the reducing action of the cathode and the nascent oxygen produced electrolytically must be brought into intimate contact with the material to be oxidised. In practice a high density cathode current is used, the cathode being a simple iron point immersed in the liquid to a depth of a few mm only; the size of the anode surface (for which a platinum band is used) is determined by the consideration that as little as possible of the evolved oxygen shall be liberated, the nascent gas being utilised. Cells without diaphragms are used at present, the anodic current density being 0.08 to 0.1 amps./sq. cm.; a cathode density of 0.85 amps./sq. cm.; a current voltage of 2.8; a working temperature of 60° C. Under these conditions the current efficiency is 55 per cent., and the current consumption 0.8 to 0.9 KwH/Kg permanganate. One other report that must be mentioned is that produced at the order of Congress by the U.S. Department of Agriculture upon the manufacture and use of sodium chlorate. Again, the manufacturing method recommended is electrolytic. The reactions which take place in the electrolytic cell are summarised as follows:

$$6\ \text{Faradays} + 6NaCl + 6H_2O \rightarrow \underset{\text{catholyte}}{6NaOH} + \underset{\text{anolyte}}{3H_2 + 3Cl_2} \quad (1)$$

$$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O \quad (2)$$

$$2Cl_2 + 2H_2O \rightleftarrows 2HOCl + 2HCl \quad (3)$$

$$NaOCl + 2HOCl \leftarrow NaClO_3 + 2HCl \quad (4)$$

$$4NaOH + 4HCl \rightarrow 4NaCl + 4HO \quad (5)$$

Overall equation:

$$NaCl + 3H_2O + 6\ \text{Faradays} = NaClO_3 + 4H_2O \quad (6)$$

Efficient Production of Chlorate

For the most efficient production of chlorate, the pH of the cell liquor should be controlled to ensure the presence of hypochlorous acid which by interaction with sodium hypochlorite (equation 4) forms sodium chlorate. The overall equation, 6, gives the primary basis of cost calculation, and it will be seen that theoretically 1,100 lb. of salt should produce 1 ton of chlorate. In practice 1,150 lb. of salt are needed, this figure being apparently determined from the operation of a pilot plant. The estimated production cost per lb. of $NaClO_3$ is 1.23 cents. When operating the process, each cell was charged with a solution containing 300 g of NaCl/litre, and the current was passed until the chlorate concentration was 525 g/litre, the concentration of the unconverted salt being 125 g/litre. During electrolysis it was necessary to add salt or brine to maintain the salt concentration and the liquor volume and to avoid loss of current efficiency. Small amounts of calcium chloride and potassium bichromate were added to inhibit corrosion and reduction of the chlorate at the cathode. After switching off the current, the liquor was transferred to steam-jacketed settling pans in which graphite particles settled out at 80 to 90° C., and reactions involving the formation of chlorate from hypochlorite were completed. The liquor was allowed to settle thus for 6 to 12 hours and was filtered through sand and evaporated to recover the chlorate from the liquor.

The Fertiliser Industry

There is little of special interest to report in the fertiliser section of the heavy industries. Renewed attempts are being made to find remunerative means of disposing of by-product ammonia. Just at present, the price enables some small profit to be made, but Mr. Holton, Chief Engineer of the Manchester Corporation Gas Department, has reported interesting experiments in which crude liquor was applied directly to crops with good results. No movement towards the establishment of regional centralised ammonia works by the gas and coke oven industries has yet been forthcoming, but there is undoubtedly an extension in the quantity of concentrated liquor produced. Attempts are reported to encourage the production of large crystals in by-product ammonia saturators. In a plant in operation at Lutterade (c.f. Berkhoff, *Chem. Met. Eng.*, July, 1937) it has been found that metallic impurities such as iron and aluminium (but not arsenic) adversely affect the size and shape of the crystal and the acidity of the bath should be kept constant and low. Phosphoric acid (or phosphates) is added to the bath to precipitate all the iron, aluminium and chromium, the amount being sufficient to correspond to the trivalent iron content, and at the same time the acidity is adjusted to be below 1.5 per cent. The precipitate is removed with the crystals and a moderate excess of phosphoric acid has no effect. Without phosphoric acid addition a high acid content is needed to keep the impurities in solution. The size of crystal produced under these conditions is said to be 77.5 per cent. above 0.5 mm and 98 per cent. above 0.2 mm screen. Under the old conditions with 6 per cent. acidity the bath produced a crystal having a ratio of length to breadth of 10:1; under the new conditions with ½ to 1 per cent. acidity, the ratio was 1.5 to 1.

In conclusion, it is recognised that considerations of space prevent anything like an exhaustive review of the technical work done in the heavy industry during the year, and the most that has been possible has been to call attention to a few interesting publications.

The Pharmaceutical Society of Great Britain

Review of Major Activities

THE number of pharmacists on the registers of pharmaceutical chemists and of chemists and druggists on December 31, 1936, was 22,977: this was an increase of 549 compared with the number on the registers on December 31 in the previous year. The number of premises registered in the Register of Premises was 15,220 in June, 1937.

In February the Council approved the plans for the Society's new headquarters in Brunswick Square. The plans, subject to minor modifications, have since been approved by the London County Council. Demolition of the houses on the site will probably commence early in 1938.

The Council have appointed a Committee of Inquiry "to consider the conditions under which pharmacy is practised in Great Britain and to report upon changes that are desirable, together with the means, whether by Act of Parliament or otherwise, to be adopted for effecting them."

The twenty-first edition of Volume I of Martindale's Extra Pharmacopœia was published during the year, and the twenty-first edition of Volume II is expected to be published in the autumn of 1938.

The new catalogue of the Society's library has recently been completed and consists of 20,336 volumes. The catalogue discloses that the library contains rare books such as the Herbarius Patariæ, 1485, Gerard's Herball, 1633, and the "Secretes of Alexis," 1560. Approximately 550 volumes have been added to the library during 1937.

Professor J. H. Burn has resigned his appointment of Dean of the Society's College and Professor of Pharmacology to take the Chair of Pharmacology at Oxford. Mr. H. Berry, University Reader in Pharmaceutics, has been appointed Dean, and Professor J. H. Gaddum has been appointed Professor of Pharmacology.

The British Pharmaceutical Conference held its seventy-fourth annual meeting at Liverpool, the chairman's address by Mr. T. E. Lescher being entitled "Pharmacy To-day—Its Responsibilities." Scientific papers were communicated on the pungency of capsicum, the colorimetric determination of morphine, the value of compound tragacanth powder as a suspending agent and on a number of other subjects of importance pharmaceutically.

The Nitrogen Industry in 1937

By
E. B. MAXTED, D.Sc., Ph.D., F.I.C.

Dr. E. B. Maxted.

WHILE the world nitrogen consumption during 1936 rose to a new high level of over 2,400,000 metric tons,[1] the productive capacity of existing plant is still greatly in excess of this figure; and it has been stated by Lord McGowan, at the annual meeting of Imperial Chemical Industries, Ltd., that a part of the hydrogen plant normally used for ammonia has now been diverted for use in connection with petrol production. This position, as far as this country and (to some extent) Germany are concerned, is in some degree due to the operation of nitrogen fixation plants in countries which previously imported larger quantities of nitrogenous products. Thus, the present productive capacity of Japan is reported to be about 2,230,000 tons of ammonium sulphate per annum, with an actual production of about 1,750,000 tons; and, under the present conditions in Japan, a decree has been issued ordering all nitric acid factories to produce at their full output. Prices remain very low; and, under the German four-year plan, the domestic prices of nitrogenous fertilisers in Germany have been reduced by about 30 per cent., retrospective to January, 1937, in accordance with the policy of expanding and encouraging the agricultural demand. It has, further, been reported[2] that the seasonal increase in nitrogen sales in Germany during the summer monthg has been greater than in recent years. According to reports, the sale of Chilean nitrate during the year ending June, 1937, increased by about 16.7 per cent., the production increasing by 7.6 per cent. with a corresponding reduction in stocks.

Of the papers which have been published during the past year, a relatively large proportion, dealing with various aspects of the field, are due to Russian workers. This intensive development is to be understood on grounds of the very large potential agricultural market in that country as well as for reasons connected with agricultural independence. With the above exception, the year's publications relative to the nitrogen industry are probably less in number than is usual. This position, as has been pointed out in previous reports, is largely a symptom of stable and well-established technique in which radical changes no longer easily occur.

Synthesis of Ammonia

As is well known, the activity of ammonia catalysts varies greatly with the temperature and method of reduction. S. S. Latschinov[3] has studied from this standpoint the influence of temperature and other factors in the reduction of iron-potash-alumina catalysts by nitrogen-hydrogen mixtures. Complete reduction takes place below 475-500°, the time necessary for reduction being given by the relationship $yx^n=k$, in which y is the temperature, x the time, and n and k constants for a given pressure and rate of gas flow. In further work Latschinov and Vedenski[4] have examined the influence of temperature, pressure and gas rate on the activity of catalysts prepared from magnetite. They recommend a gradual rise from 375 to 500° during reduction, at a pressure of 100 atm. and with a space-velocity of about 20,000. It is usual, in some methods of working, to increase gradually the partial pressure of the hydrogen in the nitrogen-hydrogen mixture as reduction proceeds.

M. J. Rubanik, T. V. Zabolotzki and M. T. Rusov[5] have re-investigated the activating effect of molybdenum on iron-alumina catalysts. They recommend fusion in an electric furnace, in agreement with established technique for preparing iron-alumina-potash and similar catalysts; and they state that fused catalysts of this nature possess greater activity when reduced and used under normal working conditions than catalysts of similar composition which have not previously been subjected to fusion. This is probably due to inter-lattice penetration of the iron oxide and the alumina, with formation of a spinel, by which means the promoter becomes intimately dispersed throughout the iron in such a way as to prevent effectively the growth of iron aggregates. The alumina is regarded as a support rather than as an activator.

A certain amount of work relative to the production and purification of synthesis gas has appeared. Thus P. Sakmin[6] has described the preparation of gas suitable for the synthesis of ammonia by a method of the type involving the low-temperature treatment of coke-oven gas under special conditions. For details reference should be made to the original paper. Special procedure for the removal of carbon monoxide from nitrogen-hydrogen mixtures is claimed by F. Porter.[7] The process involves step-wise scrubbing with ammoniacal cuprous solutions. Another paper dealing with purification is due to A. V. Avdeeva,[8] who recommends, as a pre-catalyst for the removal of oxygen, pumice soaked in a mixture of nickel nitrate and aluminium nitrate, the mass being reduced with hydrogen at 300-400° C. The synthesis of ammonia is extremely sensitive both to oxygen and to water; and further work on the inhibitive effect of water in the synthesis has been carried out by V. P. Kamzolkin and V. D. Livschitz.[9] 0.01 per cent. of moisture in the synthesis gas is sufficient to depress considerably the ammonia yield in the presence of an iron catalyst; and the inhibitive action is stated to be greater with a relatively inactive than with a very active catalyst. This is in conformity with the difference in the surface-mass ratio. The use of moist gas, further, causes a rise in the optimum temperature for the synthesis.

Nitric Acid and Nitrates

The loss of platinum during the oxidation of ammonia by an oxygen-steam mixture has been examined by I. E. Adadurov, V. I. Atroschenko and V. I. Konvissor.[10]. Under conditions of working in which the platinum gauze was maintained at a temperature of about 900°, the loss was about 2.4 grams of platinum per ton of nitric acid produced. Less work than usual has been published on catalysts for ammonia oxidation; but the Du Pont de Nemours Co. and Baker and Co.[11] have protected the use for this purpose of alloys containing a platinum metal and coated with substantially pure platinum. Several publications deal with the production of concentrated nitric acid from the reaction gases derived from the oxidation of ammonia. Thus, in a method described by S. L. Handforth and J. N. Tilley,[12] these reaction gases are cooled under pressure to remove the bulk of the nitrogen peroxide and passed to the centre part of a tower which is fed with dilute nitric acid.

The Du Pont de Nemours C.[13] claim a process involving cooling to remove water, followed by compression, during which the greater part of the nitrogen peroxide is liquefied. The uncondensed gases are used for enriching nitric acid under special conditions at a pressure of about 20 atm. A process of somewhat similar type has been described by G. P. Davies and Imperial Chemical Industries.[14] The gases, after being cooled to remove water, are absorbed in 90 per cent. nitric acid at 3-5 atmospheres and at 0-10° C. The resulting solution is oxidised with air at a high pressure with addition of dilute nitric acid. The Bamag-Meguin A.-G.[15] have protected a method involving the absorption of nitrous gases in

highly concentrated nitric acid under special conditions. The reaction gases from ammonia oxidation are cooled quickly to remove water, allowed to oxidise to nitrogen peroxide, again cooled with separation of dilute nitric acid, and the gases absorbed in concentrated acid, as above.

A further contribution to the direct production of concentrated nitric acid by the interaction of dilute acid, oxygen and liquid nitrogen peroxide under pressure has been made by P. I. Pronin;[16] and A. V. Tichonov and J. V. Korzinkina[17] have examined the manufacture of nitric acid of high concentration by distilling nitric acid to which phosphorus pentoxide has been added. An addition of 0.5-1g. mol. per g. mol. of water is stated to result in the production of a 97 per cent. acid. Finally, the formation of nitrous oxide, in place of nitric oxide, by using a manganese-oxide-bismuth-oxide catalyst has been examined by V. F. Postnikov, L. L. Kuzmin and N. K. Tzalm.[18] It is stated that yields up to 88 per cent. may be obtained at a working temperature of 200-300°.

Special Procedure in Nitrate Manufacture.

Turning to the manufacture of salts, M. A. Minovitsch[19] has investigated the preparation of sodium nitrite from soda and oxides of nitrogen, and C. F. Weston[20] has described special procedure in the production of nitrates by the interaction of nitrous gases with sodium carbonate: further, K. Haase and H. Werth[21] have discussed the manufacture of potassium nitrate by the action of ammonia oxidation gases on sylvinite. An interesting investigation of the production of potassium nitrate from potassium chloride and nitrogen peroxide in the form of gases from the oxidation of ammonia has been carried out by D. L. Reed and K. G. Clark.[22] A stepwise counter-current process, with oxidation chambers between the reaction beds, led to complete reaction, one-half of the nitrogen oxides being converted to potassium nitrate and one-half to nitrosyl chloride. According to a patent specification of H. Pauling,[23] sodium nitrate is made by the interaction of sodium chloride and nitric acid in the presence of steam and under reduced pressure. It is stated that no chlorates or nitrosyl chloride are formed. The hydrochloric acid produced is removed continuously by distillation.

The manufacture of calcium nitrate from limestone and nitric acid has been discussed by N. A. Jatsuta, L. M. Kantorovitsch and V. A. Klevke;[24] and a process representative of the preparation of nitrates by double decomposition is claimed by the Interessen-Gemeinschaft.[25] Sodium chloride, in suspension in a saturated solution of a mother liquor consisting of ammonium chloride and sodium nitrate, is caused to react with ammonium nitrate in the same medium. Sodium nitrate is separated from the reaction mixture by cooling and flotation. Little new has appeared on the subject of ammonium nitrate; but an apparatus in which the heat of neutralisation is used for evaporation has been described by L. M. Lashnik.[26]

Ammonium Salts

The production of solid mono- and di-ammonium phosphates by stripping ammonia-containing gases, such as coke-oven gas, by means of ammonium phosphate solution containing phosphoric acid, under special conditions, is dealt with by J. E. Morse;[27] and an interesting method for the direct production of ammonium sulphate from pyrites and other sulphur-containing materials, including spent gasworks purifying mass, is claimed by H. Heimann.[28] The material used is treated with aqueous ammonia at a high temperature and pressure (*e.g.*, at 200° and at 40 atm.) in the presence of oxygen. Several patents have been published relative to the crystallisation of ammonium sulphate. Thus, A. von Kreisler[29] claims the use of small quantities of urea in the formation of coarsely crystalline sulphate, and a somewhat similar process has been described by the Interessen-Gemeinschaft,[30] who state that the production of coarse crystals of ammonium chloride—from sodium chloride and ammonium hydrogen carbonate—may be promoted by the presence of small quantities of urea, biuret and other bodies. The general subject of ammonium sulphate crystallisation has, further, been discussed by G. Berkhoff,[31] who recommends the addition of phosphoric acid.

Miscellaneous Nitrogen Compounds

E. J. Du Pont de Nemours and Co., H. A. Bond and C. R. Harris[32] claim a process for the manufacture of hydrocyanic acid in which nitric oxide is allowed to react with a hydrocarbon in the presence of platinum supported on a refractory carrier; and A. D. Macullum[33] describes the drying of sodium cyanide solutions by the use of hot rollers on which the drying process occurs at a speed which prevents substantial hydrolysis. The purification of commercial calcium cyanamide from calcium oxide has been dealt with by V. F. Postnikov, A. C. Bronnikov and I. P. Kirillov.[34] Two methods are described, involving respectively the passage of hydrocyanic acid at 700-800° or of ammonia and carbon monoxide over the impure calcium cyanamide in the presence of alumina or carbon.

The manufacture of sodium and potassium ferrocyanides from various forms of crude cyanide, including cyanide from the Bucher process, has been investigated in considerable detail by N. A. Fleischer and N. A. Osokoreva.[35] Finally, V. F. Postnikov, T. I. Kunin and A. A. Astascheva[36] have discussed the production of a mixed fertiliser, containing phosphates and urea, from calcium cyanamide and phosphoric acid. The calcium cyanamide is treated with phosphoric acid, when the cyanamide which is liberated reacts with water to form urea. Ammonia is then added to give a mixture of ammonium and calcium phosphates.

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CYCLOHEXYL BENZENE is the main product from the condensation of benzene with cyclohexene (now available on a commercial scale) in presence of aluminium chloride, when three times the theoretical quantity of benzene is used and cooling is applied, according to Nametkin and Pokrovskaia (*J. Obchth. Khim.*, 1937, No. 6, p. 962). The by-products are liquid and solid isomers of dicyclohexyl benzene and tricyclohexyl benzene.

The Year's Progress in Analytical Chemistry

By
NOEL L. ALLPORT, F.I.C.

A REVIEW of advances in analytical chemistry entails a consideration of the subject in its application to numerous industries and to many departments of scientific research. A year's progress in so wide a field can hardly be adequately described within the limits of a short article and no claim is made for the completeness of the following brief survey.

Spectrographic Analysis

The development of spectrographic methods has been a notable feature of analytical practice during the last few years. Increased accuracy in reading the length of lines on spectrograms when applying the logarithmic sector method has been attained by Wilhelm,[1] who has devised a new eyepiece whereby it is claimed that the error in reading has been reduced to one-third of that reported with the ordinary measuring eyepiece. The logarithmic sector method of quantitative analysis, originally proposed by Scheibe and Neuhausser [2] and modified by Twymon and Simeon,[3] consists essentially in placing a metal disc with a logarithmic periphery directly in front of the slit of a stigmatic spectrograph and rotating it during an exposure, thereby causing the effective time of exposure to vary along the slit, whence the lines that are produced on the photographic plate decrease in density along their lengths and fade out at one end. The length of the lines varies in accordance with the intensity of the spectrum lines in the light source and hence is related to the quantities of the elements producing the lines.

Noel L. Allport.

The main difficulty with this method lies in determining the exact length of lines which fade towards one end. In the proposed modification of Wilhelm a reference spectrum line is removed from a spectrogram and permanently mounted beside a 20 mm. glass scale contained within the eyepiece. To effect this the original spectrogram and the glass scale are placed in water and the line, with sufficient gelatin to cover the field of the eyepiece, is cut from the plate by means of a razor blade. The scale, with the adhering film, is removed from the water, dried in the proper position and covered with a clear colourless lacquer. In this way the length of any particular line relative to the reference spectrum line is determined more accurately by simply setting the eyepiece so that points of equal density are in horizontal juxtaposition.

Microchemical Methods

In this important branch of analytical technique we find attention still being directed to the perfection and extended use of "spot" tests. Yagoda [4] has described a method for improving their application by first impregnating the absorbent paper with a solution of the reagent, drying and then "printing" the sheet with paraffin so that non-greased circles are formed where the test can be applied within a confined area. Another interesting development has been effected by Clarke and Hermance,[5] who have introduced a neatly designed capillary burette whereby it is possible to render certain "spot" tests approximately quantitative, and at the same time, to greatly enhance their sensitivity.

Improvements for the micro-analysis of gases employing the principles originally worked out by F. E. Blacet, in 1931, are reported by Seevers and Stormont.[6] Modifications have been made in order to apply the method to biological studies, and it is stated that over five hundred samples, varying in volume from 0.5 c.c. to 0.15 c.c., have been satisfactorily analysed for their content of carbon dioxide and oxygen. Blacet, in association with Volmon,[7] has extended his method of gas analysis on the microchemical scale to include a new procedure for the combustion of gases and has applied it to the determination of nitrous oxide and methane.

Colorimetric Analysis

Colorimetric analysis has lately become such an extensive subject that it is usually considered separately from microchemistry, of which it is a branch.

The useful colour test for tin using 4-methyl-1 : 2-dimercaptobenzene (toluene-3 : 4-dithiol) has been adapted by its originator, R. E. D. Clark, to quantitative work.[8] About 0.2 gram of the solid reagent is dissolved in 100 c.c. of 1 per cent. aqueous sodium hydroxide solution containing 0.5 gram of thioglycollic acid. For the determination of tin the acid solution of the metal is treated with a few drops of thioglycollic acid to ensure reduction to the divalent state, and is then diluted until it contains not more than 60 p.p.m. of tin. A measured quantity (5 c.c.) of this solution is placed in a graduated test-tube, and 1 c.c. of hydrochloric acid and 1 c.c. of a warm jelly of agar are added. The solution is heated to boiling and maintained at that temperature until the agar is in solution. After cooling, 2 c.c. of the reagent, together with sufficient water to bring the total volume to 10 c.c. are added. The tube is immersed in boiling water for 60 seconds, and the liquid is then poured into a porcelain tray (3.3 by 3.3 cm.) to a depth of 2 mm., where its colour is matched by the Lovibond tintometer using *reflected* light. The intensity of colour varies directly with the concentration of tin up to 10 Lovibond red units, which are equal to 30 p.p.m. of tin in the mixture contained in the tray. Nitroso-R salt has been applied to the colorimetric determination of potassium by Sideris.[9] Organic material to be examined is incinerated and the potassium is isolated as the cobaltinitrite salt, which is then dissolved in dilute acid and treated with sodium acetate and an aqueous solution of nitroso-R salt. The red coloration is matched by standards prepared from cobalt solutions of known strength. The test, which is delicate and reasonably expeditious should prove useful in biochemical research.

Determination of Nitrates

The colorimetric determination of nitrates using 2 : 4-xylen-1-ol (m-4-xylenol), originally introduced by Blom and Treschow,[10] has been the subject of a study by Werr.[11] Traces of nitrates are determined by mixing the suitably prepared sample under examination with sulphuric acid and adding a dilute solution of the reagent in glacial acetic acid. After maintaining at 35° C. for 30 minutes the liquid is distilled into a receiver containing dilute sodium hydroxide solution; the presence of nitrates is revealed by the formation of a yellow colour due to the action of alkali on the 5-nitro-2 : 4-xylen-1-ol which passes over on distillation. The method is capable of yielding accurate quantitative results and deserves to be more widely known.

So many valuable papers on this section of analysis have appeared during 1937 that it is difficult to offer a constructive

selection. Following work carried out many years ago by Lenher [12] it has been shown that gold may be neatly precipitated and separated from the platinum metals by hydroquinone.[13] The gold solution is evaporated to dryness with sodium chloride and acid, the residue dissolved in dilute hydrochloric acd and gradually precipitated with an excess of aqueous hydroquinone solution. After boiling for 20 minutes and allowing to cool, the gold is filtered off. If palladium is present in the filtrate it may be determined by direct precipitation with dimethylglyoxime, while platinum can be precipitated by boiling the filtrate with sodium formate after preliminary destruction of excess hydroquinone. Independently, W. B. Pollard [14] has developed an ingenious method for the micro-determination of gold by titration with standard hydroquinone solution using o-dianisidine as indicator, the end-point being marked by the discharge of the red colour. This method is applicable in the presence of many other metals. Where the quantity of gold is very small (as in the urine of patients undergoing treatment with gold salts) the metal is co-precipitated with tellurium, which is then burnt off preparatory to the titration.

In determining antimony by titration with standard bromate solution, according to Györy's method, it is customary to use methyl orange as indicator, the final disappearance of the pink colour being taken as the end-point. Szebelledy and Sik [15] have suggested the use of apomorphine hydrochloride whereby the rather uncertain end-point produced by destruction of the pink tint of methyl orange is replaced by the sharp appearance of a deep reddish-brown colour. Another organic reagent, the β-aminonaphthalide of thioglycollic acid, $C_{10}H_7NH.CO.CH_2.SH$, in which the hydrogen atom of the SH-group is replaceable by metals, has been suggested by Berg and Fahrenkamp,[16] who recommend it for the precipitation of thallium. Separation of this metal is said to be specific in alkaline tartrate solution containing cyanide, the complex $Tl(C_{12}H_{10}ONS)$ forming a lemon-yellow crystalline precipitate. Another paper on metallurgical analysis of special interest is the exhaustive study on the determination of cobalt by B. S. Evans,[17] who proposes an elegant modification of the cyanide titration.

Detection of Poison Gas

In connection with this unhappily topical subject interest attaches to investigations by Ligtenberg [18] on the detection of mustard gas. The gold chloride test due to G. A. Schröter,[19] which is specific, can be made sensitive to 4 grams per cb.m. by drawing the suspected air through a U-tube with a constricted bend containing one drop of a 0.1 per cent. solution of Schröter's gold reagent. The open end of the U-tube is provided with a dust filter and a metal funnel 10 cm. in diameter. The first appearance of turbidity in the reagent due to the formation of a yellow addition product is easily observed against a dark background, or at night-time, by means of a blue light. In a later paper [20] the same author recommends a serviceable modification of the non-specific Sudan red test for mustard gas in which a positive reaction is indicated by the formation of a blood-red colour. One part of Sudan red is ground with 1,000 parts of powdered chalk and this mixture is evenly incorporated into 3,000 parts of non-purified sea-sand. This is distributed over the area under examination, and if a positive reaction is obtained it may be confirmed by dusting over the first powder another consisting of 1 part of ferric chloride and 7 parts of ground chalk when a green colour is obtained within a minute if mustard gas is present. This reaction also detects bromo-benzyl cyanide and phenyl-carbylamine chloride which are sometimes used to disguise the presence of poison gas.

Petroleum Analysis

A paper by Kurtz and Headington [21] on the analysis of light fractions is likely to interest petroleum technologists. A scheme is presented for the approximate determination of conjugated diolefins, cyclic olefins, non-cyclic olefins, aromatics, paraffins and naphthenes or saturated cyclic compounds. The special feature of the analytical plan is the adoption of a newly-proposed physical constant called the refractivity intercept. It is shown that, for a given structure, the refractive index varies linearly with the density and the refractivity intercept is the constant b in the expression:—Refractive index = 0.5. density + b.

Application of Chemical Treatment

Hydrocarbon types differ, in this respect, only in the numerical value of b and therefore are distinguishable by this constant. In the proposed scheme of analysis the density and refractivity intercept of the unknown mixture are graphically plotted with like points for not more than three hydrocarbon types of the same boiling range. In order to use this method of analysis on mixtures of more than three components, resort is made to chemical treatment which will segregate or remove three or less of those forms which can be analysed graphically. When no more than three hydrocarbon types are displaced from the sample by the treatment, the refractive index and density of the ternary mixture removed may be calculated from those physical characteristics and the volume of the sample before and after treatment. Its composition may then be determined graphically. The chemical treatment involves removal of conjugated diolefins by the maleic anhydride method of Diels and Alder,[22] while on a separate portion of the sample all the olefines and aromatics are removed by means of sulphuric acid according to the method of Faragher, Morrell and Levine.[23] The loss in volume due to the maleic anhydride treatment serves to determine the proportion of diolefins present, while measurement of the density, refractive index and volume before and after acid treatment permits of the calculation of the density and refractive index of the ternary mixture removed by the acid and hence graphical estimation of its composition; finally, the residue, when freed from polymers, contains only naphthenes and paraffins and its composition may be closely approximated by graphical analysis using the data provided in the original paper.

Fixed Oils

A contribution which will be welcomed by all analysts concerned with the examination of these products is an improvement by Evers [24] of Bellier's [25] sorting test for arachis oil present as an adulterant in olive and almond oils. It is shown that the test as described in the *British Pharmacopœia* is unsatisfactory since many genuine oils fail to pass, and it thus becomes necessary for the analyst to conduct the laborious confirmatory test involving separation of the fatty acids. The modified test is carried out as follows:—To 1 c.c. of the oil under examination add 5 c.c. of 1.5 N-alcoholic potassium hydroxide and heat on a water bath for five minutes, avoiding loss of alcohol. Add first, 50 c.c. of 70 per cent. alcohol and then 0.8 c.c. of hydrochloric acid (sp.gr.1.16). Warm to dissolve any precipitate, slowly cool at the rate of 1° C. per minute stirring with a thermometer meanwhile. With olive oil, if a turbidity appears before the temperature has fallen to 9° C. the usual confirmatory test for arachis oil must be applied; otherwise this adulterant may be regarded as absent. For the detection of arachis oil in almond or apricot-kernel oils the same test is applied, excepting that with genuine products clouding should not occur above a temperature of 4° C.

Another analytical paper of interest concerns tung oil. As the drying property of this oil is chiefly due to its content of eleostearic acid, it appears that a direct determination of it would give a better commercial evaluation of the oil than any consideration of constants. A method has now been devised by Ku[26] which depends upon the fact that, whereas oleic acid is readily soluble in 76 per cent. by volume ethyl alcohol at 0° C., eleostearic acid is only dissolved to a very slight extent. The isolated fatty acids from the oil are dissolved in warm 76 per cent. alcohol and the solution cooled to 0° C. for several

hours, when the cream-like crystals of eleostearic acid are collected, washed and titrated in the usual way.

Towards the latter part of 1936 an important advance in the chemical evaluation of aneurin, or vitamin B_1, was made by Jansen.[27] The vitamin is oxidised with potassium ferricyanide to thiochrome, rendered alkaline with sodium hydroxide, agitated with iso-butanol and the resulting extract exposed to filtered ultra-violet light. Under these conditions vitamin B_1 yields a brilliant violet fluorescence, which Jansen measured by means of a photoelectric cell connected to a galvanometer. Karrer and Kubli [28] have improved and simplified the method so that the vitamin may be determined by direct visual observation. The standard is prepared by transferring 0.2 c.c. of an aqueous solution of vitamin B_1 hydrochloride containing 5 International Units per c.c. (1 gram of the solid is equivalent to 440,000 International Units) to a 25 c.c. graduated glass stoppered measuring cylinder, adding first 0.05 c.c. of 1 per cent. aqueous solution of potassium ferricyanide and then 3 c.c. of 10 per cent. sodium hydroxide solution. After agitating for 90 seconds 12 c.c. of iso-butanol are added, the mixture is shaken vigorously for 2 minutes and allowed to separate, and 4 c.c. of the iso-butanol filtered into a test-tube; this produces the standard fluorescence. Samples for examination are similarly treated and, if the fluorescence produced is greater than that of the standard, the iso-butanol is diluted with more of the same solvent until 4 c.c. is equal to the standard containing 1 International Unit in 12 c.c.; if the fluorescence is weaker, a larger quantity of sample is submitted to the test.

Examination of Foods

In some countries the use of *p*-hydroxybenzoic acid, its sodium salt or its esters is permitted for purposes of preserving food and it is therefore sometimes necessary for British analysts to examine samples of imported canned goods for these substances. A useful scheme for their detection and determination, with special reference to their distinction from salicylic and benzoic acids, has been worked out by Edwards, Nanji and Hassan.[29] The essentials of the method rest upon the rose-red colour produced by the addition of Millon's reagent to dilute solutions of the ammonium salt of *p*-hydroxybenzoic acid. Under similar conditions salicylic acid gives an orange-red colour, but the presence of the para-acid may be established by evaporating a mixed solution of the ammonium salt and copper sulphate to low bulk and allowing it to cool, when characteristic crystals of the sparingly soluble copper *p*-hydroxybenzoate separate. The colour with Millon's reagent serves for making colorimetric determinations, the most suitable range of standards containing 0.1 to 1.0 mg. of the acid as neutral ammonium salt in 20 c.c. to which 2 c.c. of reagent are added followed by heating in a boiling water-bath for two minutes and, finally, dilution to 50 c.c. Full details for preliminary isolation of the preservatives from various foods are given.

Another paper likely to prove useful to those engaged in food analysis is that due to Hamence,[30] who describes a comprehensive plan for the separation and determination of metallic impurities in foodstuffs. Those concerned with the examination of distilled liquors will be interested in the coordinated system of colour reactions using vanillin, salicylaldehyde and *p*-dimethylamino-benzaldehyde for the determination of higher alcohols, which has been proposed by Penniman, Smith and Lawshe.[31] According to these investigators the well-known Allen-Marquardt dichromate process yields irregular results which are always below the true values.

Drugs and Pharmaceutical Preparations

The method for the determination of acriflavine and the related compounds originated by Powell and Hall [32] has been adapted to the examination of medicated gauze and pharmaceutical preparations containing fats, gelatin and glycerol.[33] Details are presented for the preliminary isolation of the dyestuff and the solution thus obtained, containing from 0.02 to 0.2 gram of the diaminoacridine derivative, is diluted to 200 c.c. and rendered faintly acid to Congo red paper. After the addition of 1 gram of sodium acetate an excess of M/50 potassium ferricyanide is added, the mixture allowed to stand thirty minutes and then filtered, the precipitate being washed with a little water. The excess ferricyanide is now determined by adding 5 c.c. of hydrochloric acid (sp.gr.1.16), 1 gram of sodium chloride, 0.5 gram of potassium iodide and 5 c.c. of 30 per cent. zinc sulphate solution, then, after standing for three minutes, titrating with N/100 sodium thiosulphate. A control is conducted at the same time. Each c.c. of M/100 ferricyanide is equivalent to 0.00888 gram of acriflavine, 0.00779 gram of euflavine, or 0.00921 gram of proflavine.

Detection of Barbiturates

For the detection of barbituric acid derivatives Zwikker's cobalt test [34] as modified by Bodendorf [35] is invaluable, but, as the method is a generic one for the whole group, a positive result implies a further examination to ascertain the identity of the particular acid. Jespersen and Larsen [36] have published a useful paper describing the preparation of a series of derivatives with xanthydrol and another with *p*-nitrobenzyl chloride. The melting points of these compounds, together with the parent acid, are given for twenty barbiturates. To conclude this review reference may be made to an interesting method proposed by del Boca and Remezzano[37] for the characterisation of the acetyl group in medicaments by application of the "lanthanum blue" reaction. Dilute sulphuric acid is added to the substance to be tested, the mixture distilled and lanthanum nitrate solution added to the distillate; the mixture is then treated with solution of iodine and a slight excess of ammonia when the presence of acetic acid is revealed by the formation of a blue colour.

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Colloid Chemistry in 1937

By
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THE year has been notable for several important symposia serving to focus current views and research on selected topics. The Faraday Society's subject was: "Properties and Functions of Membranes, Natural and Artificial." Thirty-two papers were contributed[1] and were summarised by Rideal. The British Section of the International Society of Leather Trades' Chemists discussed in twenty papers: "Wetting and Detergency. Scientific and Technical Aspects." A monograph was published[2] by A. Harvey, collecting the papers and discussions. Four contributions to the *J. Soc. Chem. Ind.*[3] dealt with Films: (1) the mechanism of film formation of tars; (2) film formation with cellulose derivatives; (3) the structure and mechanical properties of protective films; (4) the structure and electrical properties of protective films. (The preparation and properties of collodion membranes have been described by Spiegel-Adolf).[4]

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The papers presented at the 14th Colloid Symposium, Minneapolis in June, 1937, are published[5] in the *J. Phys. Chem.*, October, 1937. They are:—(1) "Some Recent Work on Gels" (Freundlich). The treatment included structure; sol-gel transformation; silicic acid gels; thixotropic transformation; dilatancy; rheopexy; hydration; Hofmeister ion series. (2) "The Thixotropic Behaviour and Structure of Bentonite" (Hauser and Reed). A study in three parts: (a) production of the particle size; (b) study of the structure of the bentonite particle; (c) study of the thixotropic behaviour as a function of particle size. (3) "The Colloid Properties of the Clays as Related to their Crystal Structure" (Marshall). (4) "The Sorption of Chlorine by Silica Gel" (Reyerson and Wishart). (5) "Determination of Ice-Water Relationships by Measurement of Dielectric Constant Change" (Alexander and Shaw). This presents a method based upon the change in dielectric constant which occurs when water in the liquid state forms ice or when ice melts to form liquid. The material to be studied is made a part of the dielectric of an electrical condenser. (6 "The Adsorption Nature of Chrome Tanning" (Cameron and McLaughlin). Chrome tanning is a typical reversible adsorption process rather than what would be termed stoichiometric. (7) "Properties of Built-Up Films of Barium Stearate" (Miss Blodgett). Describes the use of interference colours to measure small changes of film thickness, and a method whereby monolayers having a thickness of 5A or more are made visible to the eye and measurable with a probable error of 2.5A without the use of optical apparatus. The properties of barium stearate films containing copper and some properties of skeleton films are discussed. (8) "Built-Up Films of Protein and Sterol" (Bull). (9) "Certain Colloidal Reactions of Cellulose Membranes" (Farr). (10) "Colloid Chemistry in Paper Making" (Rowland). (11) "The Bonding Force of Cellulosic Materials for Water" (Stamm and Hansen). (12) "Studies in Drop Formation as Revealed by the High-Speed Motion Camera" (Edgerton, Hauser and Tucker).

Surface Films

The importance of investigations on surface films, especially built-up films of the Langmuir Blodgett type, cannot be overstated, and McBain, Ford and Wilson[6] have described new methods for their study. Harkins and Anderson[7] describe an easily-built apparatus, a simple and accurate film balance of the *vertical* type. With it they investigated the tight packing of a monolayer of stearic acid by calcium ions which compress the fatty acid ions of the film and eliminate the expanded region obtained with the stearic acid alone. Other papers deal with: the viscosity of monomolecular films;[8] the examination of monomolecular films by electron diffraction;[9] the structure of Langmuir-Blodgett films of stearic acid;[10] [11] monomolecular films of α-aminostearic acid, stearic acid and heptadecylamine.[12]

In an important contribution, Langmuir and Schaefer[13] summarise three years' work on the properties of monolayers of stearic acid on water containing low concentrations of metallic salts at various *p*H values. Photographs show the modification of a crystallised monoskim of pure stearic acid by the adsorption of aluminium from water containing 1 part of Al in 2 billion parts of water. Simple methods for the visual observation of the modification of monolayers are detailed.

According to Langmuir, Schaefer and Sobotka[14], monolayers (16.6-17.9A) of several sterols and the corresponding *epi*-sterols can be built up as multilayers on Cr plates. Adsorbed films of digitonin on such monolayers exhibit specificity. Digitonin from a substrate solution penetrates between sterol molecules in a monolayer on the surface and causes an expansion to about double area even against a pressure of 30 dynes/cm.

Proteins

Brouhult[15] has sent a most important letter to *Nature* concerning the splitting of the hæmocyanin molecule by ultrasonic waves of frequency = 250,000 per sec. Fragments of the protein were uniform (monodispers) and were equal to $\frac{1}{2}$ and $\frac{1}{8}$ of the molecule, whose original molecular weight = 6,740,000. These fragments do not, upon a change of *p*H from 7.2 to 6.2, show any tendency to recombine to the original molecule; their electrophoretic properties were not changed by the treatment.

A method has been developed for applying the phase rule to systems of several protein components in serum.[16] The globulin fractions so investigated are apparently homogeneous substances. Bailey[17] discusses the sulphur distribution of proteins, while Todrick and Walker[18] give a method for the determination of SH groups in proteins, important in studying, *e.g.*, denaturation. They measure the amount of oxidation-reduction indicator (phenolindo-2:6-dichlorophenol) reduced by a known weight of protein, the indicator being standardised against cysteine.

The intermolecular forces of proteins and the action and dependence of such forces upon the size and the constitution of the chemical molecule are dealt with by Frankel[19] in his paper on the behaviour of peptides in aqueous solutions. Peptides which are built up of associating α-amino-acids only, show association in solution; peptides built up of both associating and non-associating amino-acids are not associated in solution. This work should be compared with Belton's[20] on the effect of amino-acids on the surface tension of sodium chloride solutions.

When myosin is dehydrated, it becomes insoluble.[21] The number of detectable SH groups in the protein is, however, unchanged. In this respect coagulation by dehydration differs from coagulation due to other means, but resembles

the coagulation that occurs in muscle during rigor. The surface denaturation of egg albumen, so important in food chemistry, has been thoroughly investigated by Bull and Neurath,[22] while the whipping ability of soybean proteins has been observed[23] to be remarkable, especially at concentrations of 7-8 per cent. and at *p*H values well beyond the isoelectric point. Other communications deal with: the influence of the electrolyte content of the medium on the properties of completely spread protein films;[24] the globulins;[25] the scattering of light by protein solutions.[26]

Protein Structure

Of tremendous interest just now is the question of protein structure and this formed the subject of a symposium in September at the British Association meeting.[27] Important to note are communications by Astbury[28] ("Relation between 'Fibrous' and 'Globular' Proteins"), Wrinch[29] ("Nature of the Linkages in Proteins") and Mark and Philipp[30] ("X-Ray Study of Protein Structure.")

Miss Wrinch[31] has developed the cyclol hypothesis of protein structure and several notes have appeared thereon. Under the title: "The Cyclol Hypothesis and the 'Globular' Proteins" she has extended the theory to account for the existence of space-enclosing or 'globular' proteins. No abstract can do justice to this theory and the reader is referred to the original publications.

Laboratory Methods

Several new methods come from Svedberg's laboratory at Upsala. Thus, there is an analytical measurement of ultracentrifugal sedimentation,[32] specially useful for studying enzymes, antibodies and mixtures of carbohydrates and proteins.

Tiselius has given a method for investigating the chemical homogeneity and the separation into main constituents of mixtures of proteins and other high molecular compounds.[33] He has also developed[34] a new apparatus for the electrophoretic analysis of colloidal mixtures. A very considerable increase is possible in the applied E.M.F. by a change in shape of the familiar U-tube and by working at 4° C. (which reduces the risk of heat convection currents).

The electrokinetic behaviour of charcoals in aqueous solutions of organic acids has been followed by Frampton and Gortner.[35] They found that activation apparently does not affect the electrokinetic properties of charcoal. The migration velocity of graphite and diamond dust showed speeds of the same order of magnitude as the more highly activated carbon. An unusual topic concerns the electrostatic response of pigments. Reising[36] has published interesting photographs which show that pigments suspended in different types of vehicles and placed between electrodes under an E.M.F. of 450-volt, D.C. exhibit an electric charge the nature of which depends on the liquid medium. In general, polar-nonpolar compounds cause pigments to exhibit + *or* − charge, whereas in nonpolar vehicles, the pigments exhibit a simultaneous + *and* − charge.

Soaps

In treating of the surface tension of aqueous soap solutions as a function of *p*H value and salt concentration, Long, Nutting and Harkins[37] deal with sodium laurate and sodium nonylate. The surface tension is relatively high in basic and low in neutral solutions. This agrees with the idea that the long chain paraffin ions together with the electrostatically held positive "gegen" ions are adsorbed from the strongly basic solutions, while the much more surface-active acid is the more adsorbed from the slightly basic or neutral solutions.

Other papers deal with: the existence and nature of acid soaps;[38] viscometry of solutions of sodium oleate;[39] the peptisation of aqueous soap solutions;[40] metallic soaps for thickening mineral oils.[41] Cupplles[42] extends his earlier work on the wetting and spreading properties of aqueous solutions, using mixtures of NaOH with *n*-caproic, *n*-caprylic, *n*-capric, lauric, myristic, and palmitic acids. The curves show that the surface tension decreases with increase in molecular weight of the fatty acid. The curves for the palmitate, myristate, oleate, laurate, and *n*-caprate are close together and form a rather distinct group from the curves for the *n*-caprylate and *n*-caproate, which are more widely separated from each other and from those of the acids of higher molecular weight.

Wetting

Rhodes and Wynn[43] have studied the effect of salts on the detergent action of soap. The maximum effect was at pH = 9.66, and the addition of NaCl, Na_2SO_4 or Na_2HPO_4 at first increases and then decreases the maximum detergent effect.

Synthetic aliphatic penetrants are described by Wilkes and Wiskert,[44] who deal with the "Tergitols" (sodium secondary-alcohol sulphates). Their surface activity differs markedly from that of the primary polar compounds of fatty origin, and they possess unusual powers of wetting and penetration and stability towards calcium hardness.

Powney and Addison[45] have two papers under the general theme of the properties of detergent solutions: (1) "The Surface and Interfacial Tensions of Aqueous Solutions of Alkyl Sodium Sulphates"; (2) "The Influence of Added Electrolytes on the Surface Activity of the Higher Alkyl Sodium Sulphates."

Other communications on wetting include the wettability of solid surfaces,[46] wetting of charcoal,[47] activated charcoal and silica,[48] and the heat of wetting of activated silica gel.[49]

Colloid Character

McBain and Laing McBain[50] deal with the effect of departure from spherical shape on the viscosity caused by colloidal particles and large molecules. The effect of extreme departure from sphericity is too small to account for high viscosity which even 0.1 per cent. of certain colloids imparts to solvents. Here, structural viscosity is the chief factor; entanglement and local adherence of molecules and particles effectively immobilises a disproportionate amount of the solvent in comparison with the amount of colloid itself.

A very detailed account of the solubility properties of certain highly polymeric substances has been presented by Coltof.[51] There are two kinds of interaction between a liquid (simple or mixture) and a highly polymeric substances: (a) miscibility in all proportions to yield a solution or a gel, according to the fluidity of the mixture; (b) limited swelling. The former is the technically important one and its attainment requires the solvent to effect dispersion and swelling in a certain ratio and to such an extent as not to be impaired by the ballast of the solvent molecule.

The streaming of liquids through small capillaries is effected by the molecular structure of the capillary material.[52] Peptisation effects may become important.

General

Colloids of elements, chlorides, sulphides and sulphates have been prepared in glacial acetic acid.[53] Many recent papers deal with the use of ultrasonic waves, as for example, the peptisation of carbon in ether by such irradiation.[54] Wannow[55] has given a timely summary of the use of ultrasonics in research. Moll[56] has summarised recent work on aerosols (for the years 1934-1936), while the use of the Mie effect to estimate particle size has received detailed treatment by Engelhard and Friess.[57]

High molecular weight alkyl(R^1)—aryl (R)-ketones[58] are waxlike solids, insoluble in water, alcohol and acetone, but very soluble in benzene, toluene, kerosene and turpentine. Ketones containing the phenoxy-phenyl radical do not crystallise from the solvent when their solubility is exceeded, but form stiff gels of prolonged stability. They are, moreover, excellent foam preventers in boilers operating at 200 lb./sq. in.

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Improvements in Constructional Materials for Chemical Plant

By

" CHEMICAL ENGINEER "

RECENT developments in the application of metals as materials of construction for chemical plant have not been centred so much in the direct application of new alloys as in making known alloys more suitable for use by slight modifications to composition or treatment; minor changes in certain chemical processes have also allowed some of the well-established alloys to find a wider field of utility. Most new alloys are considered in due course as possible materials for the construction of chemical plant, because a very large proportion of the plant engaged in industry at the present day comes into contact with chemicals, athough not directly concerned in the manufacture of chemicals, but the most useful developments have been due to co-operation between the chemical engineer and the metallurgist. These remarks do not apply only to metals; they are also true in the case of non-metallic materials.

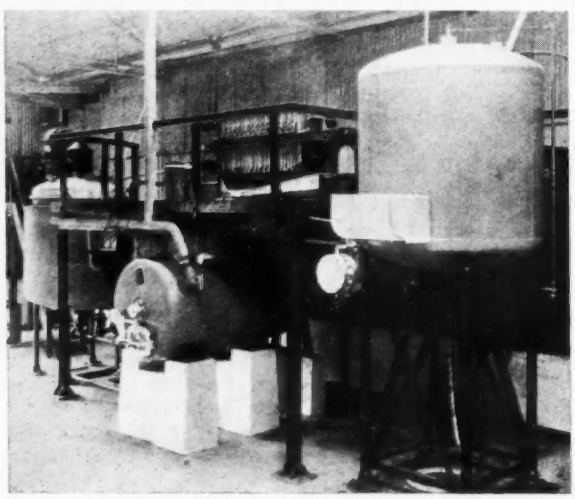
Ferrous Metallurgy

In ferrous metallurgy slight changes in composition and modified methods of treatment have been mainly responsible for opening new applications to the older alloys already well-established. For instance, in stainless steel of the 18-8 type certain deficiencies have been obviated, and it has been found generally that minor additions of other metals can considerably increase the resistance of such steels to the action of chemicals, and thereby enable these steels to be used at much higher temperatures than formerly. Even nitrogen has been found to be an addition which is capable of giving marked improvement, in that it produces a refinement of the grain of the steel. Among the lesser-known metallic additions both titanium and columbium have received considerable attention as a means of preventing intergranular corrosion. Machining qualities have been improved by the addition of selenium. One of the most recent developments which has reached the stage of practical application, however, is the use of phosphorous as an alloying agent. Cast-irons have continued to be improved by the addition of various alloying elements, mainly nickel and chromium.

The petroleum industry has derived considerable benefit from the introduction of chromium steels with the chromium content varying from one to ten per cent., and the addition of molybdenum. Such steels, and also low-carbon nickel-molybdenum steels, have found use in the construction of oil-cracking plant.

Non-Ferrous Metallurgy

In non-ferrous metallurgy interest has continued in nickel alloys and aluminium alloys, many important applications having been found in the food processing industry. Monel metal containing aluminium has improved physical properties; copper containing between 20 and 30 per cent. of nickel, as opposed to the usual Monel metal composition with 70 per cent. copper and 30 per cent. nickel, possesses an unusual degree of resistance towards corrosion; the combination of aluminium and 18-8 stainless steel has given an alloy which is especially useful for milk products. From a metallurgical aspect means for preventing the de-zincification of

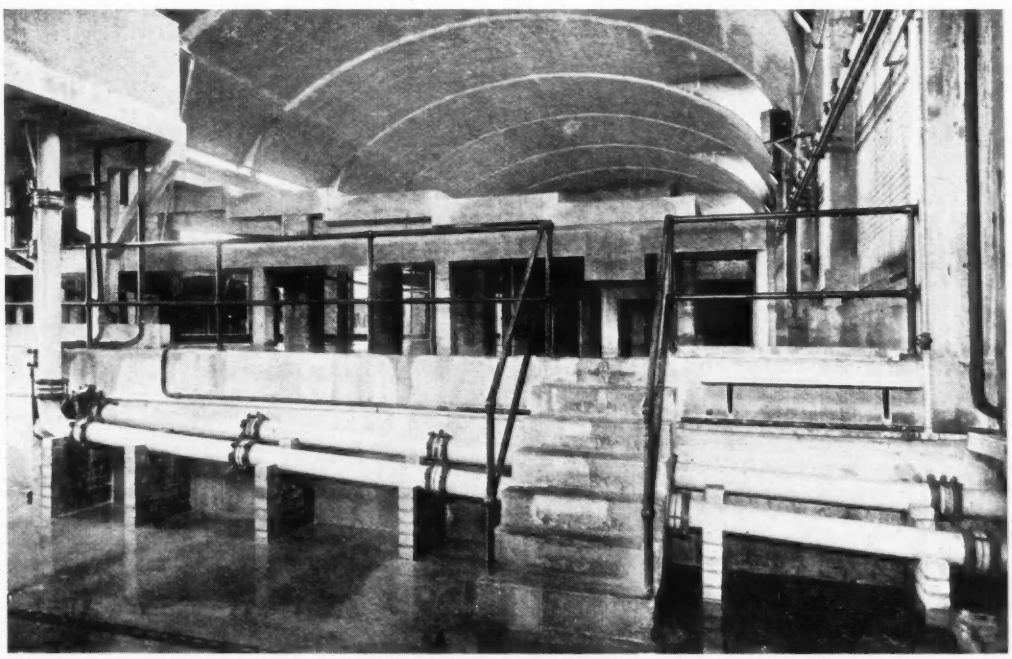


Some " Pfaudler " glass lined tanks, supplied by Enamelled Metal Products Corporation (1933) Ltd., in a plant for the production of insecticides. They comprise a 500 gal. glass lined jacketed tank used as an extraction vessel, an 800 gal. glass lined tank used as a receiving and emulsifying vessel, and a 10 gal. " junior series " measuring vessel.

acid-resisting bronzes and brasses has been a problem which has demanded considerable attention, and one which has been solved to some degree by the introduction of antimony into the alloy.

Alongside these developments certain new constructional features have arisen from the actual form in which the metal is used, *i.e.*, as special forms of sheets and tubes. The coating of common steels with stainless steel, nickel or aluminium, is typical of a case where successful application has been the result of co-operation between the chemical engineer and the supplier of plant constructional materials. For example, oil corrosion and water corrosion taking place simultaneously in particular parts of plant used in the oil-cracking industry has necessitated the production of composite metal tubing in which one surface (either inner or outer) will withstand oil corrosion while the other surface gives especially good resistance against water corrosion. Not only have two metals been used in contact; certain non-metallic materials have likewise been applied to one surface of steel—steel pipes lined with cement have been found to be very satisfactory for factory waste water which has a corrosive tendency, and steel tubes have been numerous. Even such a fitment as a spray nozzle has received attention, because spray nozzles are used under corrosive conditions and corrosion would materially affect their performance. Such nozzles are now obtainable with certain parts made of stoneware, hard rubber, stainless steel, Monel metal and other alloys to give non-clogging designs so that a constant degree of atomisation is procured at a minimum of pressure. Valves, likewise, have been made wholly of new and better alloys, or alternatively, they have been provided with an internal lining to check corrosion and thereby eliminate costly replacements and the frequent shutting down of a plant where corrosion is occasionally severe or is continuously present.

Stainless steels, considered generally as a tarnish-proof and corrosion-resisting group, and which now have a notable degree of heat resistance and freedom from scale at temperatures which would be disastrous in the case of many other metals, are still finding new applications. Their freedom from scale formation has been found especially valuable at oil refineries, and generally in chemical plants operating at high temperature and at high pressure.



Flanged stoneware pipes, made by Doulton and Co. Ltd., installed in an important plant in this country. The photograph indicates the simple manner in which they can be fitted by the use of bends and couplings. Inspection caps can be provided at all essential points, and the pipes, being made of exceptionally strong stoneware, withstand all usual pressures. Chemical stoneware resists the attacks of all acids, except hydrofluoric, in all concentrations.

coated internally or externally with glass-enamel, rubber, plastic compositions, etc., have proved useful in a variety of industrial applications.

The composition of hard and soft rubber and means to make it adhere firmly and permanently to a rigid metal surface, *i.e.*, the internal surface of a sheet steel tank, have been greatly improved within the past two years, especially for conditions where temperatures are continually fluctuating. Acid-proof chemical stoneware has been produced with increased tensile strength and still greater resistance against sudden shock or changes of temperature. Glass-enamelled steel has also received attention in this general programme of providing better materials for the chemical engineer under exacting conditions of service; this enamelled steel is being more widely adopted in cases where the purity of a product is of outstanding importance, notably pharmaceuticals, cosmetics and food products.

Developments in the actual application of materials of construction to a particular type of plant or plant fitment

De-oxidised copper is now extensively used in the form of tubes for evaporators, heat exchangers and condensing and cooling; it is suitable for all cases of heating and cooling where there is no corrosive action from the liquids which are in contact with the tubes. This de-oxidised copper has a purity of 99.9 per cent. Silver-bearing copper alloys which give high thermal conductivity, and the addition of chromium to copper for the purpose of improving the strength and hardness of the metal, are relatively new developments. Copper alloys containing 4 per cent. of nickel and 4 per cent. of aluminium have been claimed to give remarkably good resistance against corrosion under the impingement of a condensing liquid, and have been adopted for the tubes of condensers and heat exchangers at petroleum refineries. In the case of the heat exchanger this alloy proves to be advantageous by reason of its good resistance against the attack of sulphur compounds which are present in petroleum products.

Bronzes containing aluminium have continued to offer good service in contact with hot and cold sulphuric acid over an

extremely wide range of concentration (5 to 75 per cent.). Such bronzes have been shown to have the additional advantage of retaining their tensile strength up to temperatures as high as 480° C. For hydrochloric acid there are copper alloys containing silicon (1 to 5 per cent.) and manganese (1 to 2 per cent.), tin or iron; these alloys are welcomed more especially where hydrochloric acid is being handled. Everdur contains tains copper 94.4 to 96 per cent., silicon 3 to 4.5 per cent., and manganese 1 to 1.1 per cent.; Herculoy contains copper 96.25 per cent., silicon 3.25 per cent., and tin 0.5 per cent. In the United States red brass, containing 85 per cent. of copper and 15 per cent. of zinc, is gaining favour for many chemical plant uses, because it has been found to have the optimum general corrosion resistance of any of the copper alloys which are suitable for the construction of pipes and tubes.

Aluminium Alloys

Aluminium alloys now cover a very wide range of compositions with resulting variety in physical properties, which are still further modified by appropriate heat treatments. Nearly all of the alloys can be used at low temperature because they do not show any tendency to develop brittleness. Condensers and tanks for fatty acids have proved very satisfactory when made of aluminium containing a maximum of 1 per cent. of natural impurities and no additions; as an alternative, aluminium containing 1.25 per cent. of manganese can be recommended. For tartaric acid and citric acid, especially in the case of crystallising pans, high-purity aluminium is desirable. Tanks for acetic acid should be made of aluminium containing 1.25 per cent. of manganese. The same alloy is suitable for condensers on synthetic resin plant, but stills should be made of aluminium of 99.6 per cent. purity (one of the high purity chemical engineering grades).

A special application for aluminium occurs in the case of plant for preparing gelatin for the food industries. Cooking vats are made of an alloy containing manganese 2.5 per cent. and chromium 0.25 per cent.; gelatin storage tanks and screens for drying the sheets are preferably made of aluminium containing its natural impurities up to a maximum of 1 per cent. Inconel, referred to under nickel alloys, is gradually gaining favour as an alternative, because it offers complete freedom from the risk of contaminating or discolouring the gelatin, and in the form of screens is capable of resisting the severe beating of the screens to remove the dried sheets.

Nickel, Monel Metal and Inconel

Nickel and nickel alloys, here understood to include Monel metal, show no sign of being unable to find new applications. Pure nickel has a special advantage where caustic soda is handled, because it prevents iron and other metallic impurities from being extracted by the alkali, especially in the case of the tubes of an evaporator which is engaged in concentrating caustic soda liquor. Nickel owes a great deal of its corrosion resistance to its tendency to become passive under highly corrosive conditions. Monel metal has good acid resistance combined with resistance against erosion; only in the presence of an unstable and strongly oxidising agent, in conjunction with strong acidity, does it become necessary to exercise caution. A comparatively new modification, known as K Monel, contains about 3.5 per cent. of aluminium and has good corrosion resistance combined with increased strength; it acquires hardness after heat treatment, and is non-magnetic. Monel S, containing 3.5 to 4 per cent. of silicon, is suitable for castings which are subject to unusual conditions of mechanical wear.

Inconel, which is relatively new, is a high-nickel alloy containing nickel 80 per cent., chromium 13 per cent. and iron 7 per cent. It proves high resistance against corrosion by dilute organic acids and has therefore found special application in plant for food processing. Moreover, this alloy is practically free from attack by fatty acids at elevated temperature, and has proved to be superior to nearly all other materials in its resistance to the corrosive action of alkaline sulphur compounds. In another direction Inconel has given good service in the handling of photographic solutions; in contact with the ordinary "hypo" fixing solution the rate of corrosion is almost unmeasurable, and there is an additional advantage in that no deposition of silver occurs. Corrosion by a 50 per cent. solution of sodium sulphide at a temperature of 160° C. has been found to give penetrations of 0.0038, 0.013 and 0.022 in. for Inconel, Monel and pure nickel respectively, the test period being 300 hours.

Nickel-clad Steel

Nickel and nickel-clad steel are now being widely adopted in the construction of plant for the production of synthetic resins of the phenolic type, because they do not affect the colour of the product. The nickel-clad steel is used mainly for tanks for the storage and transport of the phenol. Inconel-clad steel is available in the United States.

Fine silver has now proved to be especially suitable for solutions of ammonium hydroxide, caustic soda and caustic potash at all concentrations; it is also excellent for handling citric, oxalic, formic and acetic acids.

Lead of Several Types

Lead of "chemical" quality, as specified in one of the British Standard Specifications, continues to be indispensable generally for continuous contact with sulphuric acid and liquors containing sulphuric acid. Its use is increasing in the organic chemical industry, mainly in connection with sulphonating and chlorinating plant, and also where phosphoric acid is in use.

In addition to "chemical lead" and the so-called "hard lead" containing antimony, it is now possible to obtain "tellurium lead" which has a greater tensile strength and much more general resistance to fatigue and corrosion; lead alloys containing both tellurium and antimony are also obtainable. Tellurium lead alloys may ultimately find special favour because they give longer service without repairs being necessary. Tellurium lead, and tellurium lead to which antimony has been added, are available in the form of sheets and pipes; hard antimonial lead to which tellurium has been added can be obtained as castings, including cast headers, pump casings, valve bodies, etc. A lead alloy containing 7 per cent. of tin has been introduced in the chromium-plating industry for handling chromic acid solutions at all working temperatures.

One particular instance where the new tellurium lead alloys have proved to give good service is in the case of anti-splash pipes for cooled acid coming from the Glover tower at sulphuric acid works. Here an effective life of ten to twelve months has been noted for tellurium lead, with corrosion taking place equally in all directions, whereas under identical working conditions ordinary lead pipe did not survive for more than one month. Heating coils made of tellurium lead have been proved to have two to three times the life of an ordinary lead coil in contact with phosphoric acid. For concentrating solutions of titanium sulphate, containing free sulphuric acid to the extent of 15 to 20 per cent. evaporators in the United States have been made of lead alloy castings containing lead 92 per cent. and antimony 8 per cent.

Union between steel shells and homogeneous lead linings is now so perfect that linings and shells are inseparable even under vacuum, pressure and temperature variations up to within a few degrees of the actual melting point of the lead itself.

New Additions to Cast Iron

During the last few years cast iron has been greatly improved by changes in foundry practice and by altering the basic ratios of its carbon and silicon content, but more recently particular improvements have been brought about by the addition of nickel, chromium, molybdenum and copper as alloying elements. The facility with which the iron can be cast into intricate shapes incorporating very thin sections, its general low cost, and the low cost at which it can be machined, continue to recommend it.

Pumps, valves and pipe-work, as well as reaction vessels at petroleum refineries and in other cases where sulphuric acid mixtures and caustic liquors are in use, appear to be very satisfactory when made of austenitic cast-iron. A stable austenitic structure was first developed about ten years ago by the introduction of nickel, or nickel and copper, but recent modifications in the making of such irons has greatly improved their quality and in consequence they are finding a much wider application in the chemical industry. Engaged in concentrating caustic soda from 100° to 130° Tw. the rate of corrosion of a cast-iron containing 20 per cent. of nickel is about one-eighteenth of that of a cast-iron without any nickel. With 30 per cent. of nickel the corrosion is practically negligible.

Cast-Irons Containing Nickel

Ni-resist, a cast-iron containing nickel 14 per cent., copper 6 per cent. and chromium 3 per cent., and alloy cast-irons of related composition, provide good corrosion resistance up to moderately high temperatures, but have found a notable application in pumps and valves because of the resistance which they offer against erosion. Their inherent touchness is a definite improvement on the common varieties of cast-iron, but they also acquire strength and hardness from the chromium addition. Included among these alloy cast-irons is Ni-hard, a white cast-iron of extreme hardness, containing 4 to 5 per cent. of nickel and 1.25 to 2 per cent. of chromium; it provides exceptional resistance to abrasive conditions and finds a useful application in pumps for handling gritty slurries.

A high-silicon iron containing from 3 to 4 per cent. of molybdenum is satisfactory for cold hydrochloric acid at all concentrations, but is readily attacked by hot acid except in the case of very weak solutions.

Corrosion-Resisting Steels

The production of acid and corrosion-resisting steels is now so specialised and their application in the chemical and allied industries is so diversified that only brief reference can be made to such steels in this article. Many of those of the 18-8 chrome-nickel type, here understood to include compositions ranging from chromium 16 per cent. and nickel 6 per cent. to chromium 28 per cent. and nickel 15 per cent. are now able to be welded without the need for thermal after-treatment. Molybdenum-chrome steels containing chromium 18 per cent. and molybdenum 1.2 to 1.8 per cent. have recently become important in view of the fact that their acid-resisting qualities are almost equal to the 18-8 nickel-chrome type, except in the case of low concentrations of hydrochloric and sulphuric acids. Manganese-chrome steels are also gaining favour, because they combine the good corrosion and acid resistance of the straight 18 per cent. chromium steel with the mechanical properties of 18-8 chrome-nickel steel. Recent developments in the endeavour to replace nickel by other metals include a non-austenitic chromium molybdenum steel containing 1.5 to 2 per cent. of molybdenum, and a chromium-manganese steel containing manganese 16 per cent., chromium 7 to 9 per cent., and molybdenum 1 per cent.; the former is finding special application in the construction of chemical plant in Germany.

Carbon Brick Linings

Among non-metallic materials structural carbon is coming into prominence, more especially in the United States, where it has been put to good use as a lining for paper pulp digesters and metal pickling tanks, the individual bricks being set in a carbonaceous sulphur cement. Carbon gives good resistance to strong alkalis, hydrofluoric acid and phosphoric acid. Chemical stoneware has now been so much improved that body modifications are obtainable to meet very exacting conditions in the chemical industry. Low thermal conductivity—once a notable disadvantage—has been overcome, and a much higher resistance to thermal shock has been attained. In addition, due to improved composition and refined methods of manufacture, equipment of much thinner section, and consequently lower weight and a great degree of heat transmission, has become available. The increase in thermal conductivity has been as much as 400 per cent., resistance to impact has increased 100 per cent.

Non-Metallic Protective Coatings

Among protective coatings, chlorinated rubber has been combined with plasticisers—and pigments and resins—to give new materials offering protection against nitric acid fumes and also sulphuric acid. Steel tanks coated internally with higher hydrocarbons derived fom crepe rubber are being used in the United States for the transport of iron-free caustic soda liquours for the rayon industry. Although many new plastic materials are available, phenolic resinoid plastics continue to hold the field for chemical equipment; plastic materials, however, are still unsuitable for contact with acetone, concentrated chromic acid, caustic alkalis, nitric acid, hot concentrated sulphuric acid, sodium hypochlorite and organic bases.

A remarkably high "tearing off" resistance is now procured by the use of the anode process for applying protective coatings of rubber to steal. Equipment of irregular shape can be coated satisfactorily. Rubber-like materials, such as Duprene (polymerised chloroprene synthetic rubber) and Thiokol (olefine polysulphide synthetic rubber) are gradually developing new uses, because when compared with natural rubber, Duprene, for instance, is much more resistant to the swelling action of hydrocarbons, and Thiokol gives good resistance against the action of certain volatile solvents.

Developments in the Design and Operation of Crystallisers

By HUGH GRIFFITHS

ALTHOUGH the study of crystal structure has engaged the attention of many research workers and extraordinarily fruitful results have been obtained, it is surprising that little attention has been paid to the study of crystal growth from solutions. As a chemical engineering process crystallisation is of great importance, but it is nevertheless correct to say that attempts are frequently made to design crystallising plants which display a disregard of fundamental physical principles which are comparatively easy to understand.

In 1925 the writer drew attention to the significance of the special properties of metastable solutions in industrial crystallisation processes. While certain substances had previously been produced in the "individual crystal" form and it had been shown many years ago by the investigations of Wulff, Bock and others, that crystallisation in motion did not necessarily lead to the production of small crystals, the fundamental principles had apparently not been recognised.

Investigations on the rate of growth of crystals from solution have been made by several research workers, but many of the figures recorded in the literature are probably inaccurate. Measurements of rate of crystal growth are not particularly easy to make, and the results are greatly influenced by temperature, degree of supersaturation (within the metastable region) and the presence of impurities in the solution. It is, however, safe to assume that for all practical purposes for any given solution, concentration, and temperature, the rate of deposition on a crystal surface is a definite and measurable quantity. It can, of course, be proved by physical reasoning that crystals of extremely small size must have a different solubility from large crystals, but within the range of industrial crystal dimensions an average rate of deposition

per unit area of crystal surface can be accepted. On this basis it becomes immediately possible to understand the results obtained from many different types of crystallising plant. It is a matter of experience, for example, that an ordinary salting evaporator usually produces a fine grain material whereas a vacuum crystalliser can be constructed which is to all intents and purposes, nothing but a vacuum evaporator, and will, nevertheless, produce large crystals.

Two Important Factors

It is convenient in the study of crystallisation problems to define two factors, i.e., rate of separation and surface factor. The rate of separation is the output of the plant per unit of time per unit volume of crystal-packed space. The surface factor is the area of crystal surface on which material may deposit per unit volume of crystal-packed space. It will be obvious that the output of the crystallisation plant per unit time per unit volume will be the product of the surface factor and the rate of crystal growth per unit area. The output rate is, however, also equal to the rate of separation: no matter whether the separation is effected by cooling or by evaporation. It will be clear that if the rate of separation is pushed beyond the value of the product of the surface factor and the rate of growth, metastable conditions will no longer be maintained: the solution will become unstable and a shower of fresh crystal nuclei will be produced. The shower of fresh crystal nuclei will provide a greatly increased surface and the rate of separation will, therefore, be compensated. It will be obvious that the average rate of crystal size, if the influence of attrition due to agitation be neglected, is really independent of the type of plant and that the average size of product is really only a function of the rate of separation. It will also be clear that, apart from mechanical difficulties, if increased crystal size is desired the available space in the crystallising plant must be filled with crystals as far as possible.

While these fundamental principles are easy to understand, it is surprising to find that so many crystallising plants have been built in which the obvious limits of practical possibility have been completely ignored, but several different types of plant are now extensively used which are giving excellent results. In so far as crystallisation by cooling is concerned, the simplest and best known plants are of the rocking type. These plants are cooled by evaporation from the surface of the solution and by air contact with the walls of the trough. The rate of separation per unit volume is comparatively low, and in consequence the plants are used more especially for the production of "pea" crystal products. In certain cases they can also be used for the manufacture of smaller crystals simply by increasing the rate of separation.

When water cooling is employed in conjunction with mechanical crystallisation it is, of course, necessary to prevent formation of a crystalline skin covering the cooling surfaces and stopping heat transfer. It will be obvious that this can be avoided by adopting temperature gradients which will not cause the formation of an unstable layer of solution in contact with the cooling surfaces. Careful control of the temperature difference and correct design of agitating appliances are, therefore, essential to ensure that metastable conditions are maintained, but a number of water-cooled crystallisers are now available which are operated so that no deposition takes place on the cooling surfaces.

Crystallisation by evaporation has been employed in the sugar industry for the production of coarse grained products for many years, and it is perhaps a consequence of the fact that evaporating appliances are usually purchased competitively, that in the chemical industry "salted-out" products are usually of very fine grain. Vacuum crystallisers are now, however, extensively used in which the evaporation is carried out in conjunction with crystallising vessels in which the relationship between rate of separation and surface factor may be maintained so as to produce crystals of moderate or even large size.

In some plants vacuum cooling or evaporation is employed in conjunction with steam-jet vacuum augmenters so that the final temperature of the solution may be brought down to well below 0° C., in cases where it is desired to obtain a mother liquor as free as possible from dissolved material.

Effect of Impurities

In all crystallisation processes it is necessary to bear in mind that the presence of comparatively small quantities of other dissolved "impurities" may exercise an important influence on the crystal growth. In practically all industrial crystallisation it is found that dissolved impurities may completely alter the shape of the crystals obtained. The impurities usually have the effect of retarding the growth on some of the crystal faces. An interesting example of this is found in recent methods of operating ammonia saturators, in which careful control of the concentration of ferric salts enables needle-shaped crystals to be obtained.

While it is not easy for the chemical manufacturer to change his methods, and certain courage is needed to change the appearance of industrial products which have to be sold to customers who have become accustomed to particular qualities; there are many products on the market now, in an individual crystal form, which a few years ago were exclusively made by crystallisation in stationary vessels, and in some cases the products from mechanical crystallisation plants have completely displaced the previously accepted qualities.

Review of Filtration During the Year

By

WILLIAM C. PECK, M.Sc., M.I.Chem.E., A.I.C.

THE principal source of trouble in the operation of rotary filters is the falling off in efficiency of the filtering cloth. Since all filtration is carried out by a difference in pressure between opposite sides of the filter fabric, the interstices of the fabric gradually become choked with solid particles during filtering operations. The cloth is therefore periodically cleaned by washing either by reversal of the direction of flow of the liquid or by reversal of the pressure. This reversal of pressure results in the deterioration of the fabric owing to the tension thus applied to the fibres. This disadvantage is attracting attention; thus, in the Blomco machine, the fabric rests upon a resilient layer of spongy rubber which is constantly pulsating, and its form altering with every pressure difference, so that on expansion due to release of the vacuum, the cake is split off.

A somewhat similar method of clearing the fabric interstices is shown by Burckhalter and Osborn, U.S.P.2,031,589, whereby the form of the filtering medium is altered, thus freeing the apertures of the solid material. A cylindrical grating is covered with a woven wire mesh filter medium, constructed with many longitudinal wires, but few transverse ones. One end of the filtering medium is secured to resilient material so that on application of external pressure the wires bend and on releasing the pressure the wires straighten out and eject the solid material, leaving the wire fabric clean.

The development of continuous filtration plants for materials, usually only satisfactorily handled in filter presses, is apparent. Thus rotary filters are constructed so that greater pressure than that of the atmosphere can be applied to one side of the filtering medium. The rotary filter of Schone,

Chem. Fabr. 1937, *10*, 216, consists of a rotating drum in a pressure-tight housing. The liquid to be filtered is pumped into the intermediate space at pressures of 30 to 170 lb. per sq. in., an overflow for surplus feed being provided. The filter cake is removed by a conveyor device without pressure loss. This type of filter is suitable for materials difficult to filter, such as aluminium oxide sludges. Where the feed materials are not easily handled by pumps, then travelling belts convey the liquid into the pressure chamber, which with the filtrate receiver forms one pressure unit. Thus the Standard Oil Co., in U.S.P. 2,050,007 proposes for the dewaxing of oils, an operation usually carried out in filter presses under high pressure, a continuous rotary filter consisting of a rotating drum and doctor, built inside a pressure tight shell, the upper part of which consists of the prefilt container. Gas is pumped on to the top of the prefilt container, and the wax cake is removed by a screw conveyor, the shaft of which drives the drum so that the openings requiring pressure-tight glands are reduced to a minimum.

Filter Presses

The introduction of continuous filters has stimulated the improvement in the operation of filter presses. For the feeding of the presses, weighted pumps have been introduced so designed to feed at a constant pressure and also to give a variable output at a constant pulley speed, thus the relief valves usually provided, with their attendant troubles, can be eliminated.

Folded Filters

To effect rapid filtration by extending the filter surface, Scheibler folded filters have been introduced. The filter is suitable for the final brightening of large volumes of liquid products requiring perfect clarification, and the utilisation of large filtering surfaces in a small volume has been carefully worked out.

Edge Filtration

Developments in edge filtration type filters have consisted in modifications in the shape of the washer-like elements to allow for the building of a graded filter bed. Thus in B.P. 469,152, Pickard has introduced a filter, of which about one third of the surface of each element is channelled. Similar improvements are disclosed by McLeod, B.P. 461,149, whereby the washer-like metallic plates or rings have the surfaces of one or both faces covered with radial wavy shallow grooves.

Porous Ceramic Materials

For the filtration of acid liquors, especially at high temperatures, where the corrosion problem prevents the use of cloths and woven wire cloth, considerable progress has been made in the production of porous ceramic materials. For a corrosive liquid, especially when it is desired to handle it at an elevated temperature, the filtering medium must have the properties of high permeability, chemical resistance, and mechanical strength. High firing temperatures result in materials having high mechanical strength and good chemical resistance but low porosity, while materials having the highest porosity produced with low firing temperatures have low mechanical strength. The best materials for any problem is therefore a compromise, and Schumacher materials are now available for most acid and alkaline liquids, while Doulton and Co. have a range of porous materials. A new ceramic material, Flexolith, has been introduced to take the place of filter cloth in filterpresses. The material is supplied in sheets, one millimetre thick, and is slightly flexible so that it can be used in filter presses with advantage and also the cake can be removed by scraping.

Machinery for Screening and Related Operations

Some Developments of the Past Year

ONE interesting feature in connection with the development of screening apparatus is the production of a new type of vibrating screen designed to withstand heavy usage and long years of work. It is manufactured in several sizes to carry single, double, or triple decks according to the requirements of each particular problem, and its specific feature is the introduction of special bearings of eccentric type. The smallest size of screen is made 2 ft. wide by 4 ft. long, and the largest 5 ft. wide by 12 ft. long. The largest size in the single deck type take 7½ h.p. to drive it, with 10 h.p. for the double deck, and 15 h.p. for the triple deck. The body of the screen is taken by springs at the four corners thus relieving the bearings of undue load. The driving mechanism is completely housed free from dust and damp proof. The vibrating motion given to the screen is positive, and all moving parts are in balance. A special feature of the new screen is the ease with which screen meshes can be changed.

Another advance is a light suspended screen designed for sizing lump and granular materials such as crushed stone, slag, ores, sand and gravel, and all kinds of material that are sized for special purposes either wet or dry. This machine will handle medium to fine size material with minimum variation in vibration due to load on the screen. The screen is suspended by cables and springs eliminating vibration. The mechanism can be rotated in either direction. When the machine is rotated towards the feed end, the material is slightly retarded which is desirable in certain screen operations. The screen motion is adjustable, and only two bearings of anti-friction type are employed, these being enclosed in dust proof housing.

In crushing and grinding machinery, an important development is the fitting of automatic lubrication to jaw crushers. The bearings are lubricated automatically from a grease pump having six points of lubrication, each with its own pumping unit capable of adjustment as to quantity of grease supplied to each lubrication point.

In pulverisers the use of roller bearings in place of ring oil bearings for machines of the rotary fixed or swing hammer type is being advocated. The advantages are a saving in horse power, and greater facility in starting. In the most recent instances, machines previously supplied with ring oil bearings can be fitted with roller bearings without any necessity for modification of design.

New Scientific Instruments

28th Annual Exhibition in London

THE 28th annual exhibition of scientific instruments and apparatus, arranged by the Physical Society, will be held at the Imperial College of Science and Technology, Imperial Institute Road, South Kensington, S.W.7, as follows:—January 4, 1938 (2.30 p.m. to 9 p.m.), January 5 (4 p.m. to 9 p.m.), January 6 (2.30 p.m. to 9 p.m.).

The leading manufacturers of scientific instruments will be exhibiting their latest products in the trade section. The research and education section will contain contributions from research laboratories, and experiments of educational interest. In addition, the work submitted for the craftsmanship and draughtsmanship competition by apprentices and learners will be on view.

Admission to the exhibition is by ticket only. Members of institutions and scientific societies may obtain tickets from their secretaries; tickets may also be obtained direct from the Exhibition Secretary, 1 Lowther Gardens, Exhibition Road, S.W.7.

Activity in the Dyestuffs Industry

By
R. BRIGHTMAN, M.Sc., A.C.G.F.C., F.I.C.

IT is significant that while little or no reference has been made to the dyestuffs industry in connection with industrial expansion and activity stimulated by the rearmament programme, the industry probably occupies a key position in peace time even more truly than was realised in the emergency of the great war. Its products, both colours and non-colours, are supplied to so wide a range of industries, and its intermediates are the source not merely of dyestuffs, but of rubber chemicals, medicinal products, products for the control of horticultural and agricultural pests, that the activity and progress of the industry are closely in step with that of the country as a whole. While, therefore, the industry has participated in the increased industrial activity of the country, the impact of the war in China, for example, upon the cotton and textile industries generally has in turn reacted upon the demands of those industries for the products of the dyestuffs industry.

Production Figures

The latest returns of the Board of Trade for the production of synthetic dyestuffs in the United Kingdom for 1936 show how remarkable has been the advance of the British industry under the protection of the Dyestuffs (Import Regulation) Act. The 1936 output of 61,222,901 lb. represents an increase of 571 per cent. on the 1913 figure, and is also an increase of 4.2 per cent. on the previous record output of 58,713,384 lb. in 1935. Compared with 1935, the largest increase in output is in the direct cotton colours, which increased from 10,494,850 lb. to 11,443,386 lb., due to the largely increased trade in all forms of viscose rayon. The development of the rayon industry is also reflected in the output of dyestuff for acetate rayon, which has increased from 1,801,216 lb. in 1935 to 2,246,046 lb. in 1936, a figure which should also be compared with the output of 227,501 lb. in 1928, the first year for which separate figures were available. Increased outputs compared with 1935 are also reported for acid wool colours chrome and mordant colours, sulphur colours, dyestuffs for lakes, while slight decreases are reported in the production of basic dyes and oil, spirit and wax and miscellaneous colours. The significant increase in the production of vat dyes other than indigo from 4,646,504 lb. in 1935 to 5,105,001 lb. in 1936 reflects the steadily increasing demand for coloured fabrics possessing special qualities of fastness.

Total imports of synthetic organic dyestuffs in 1936 increased to 6,639,936 lb. as against 5,513,380 lb. in 1935, imports consisting almost entirely of dyestuffs not made in this country. The largest increase occurred in the vat dye group, imports of basic, lake-making and pigment dyes showing decreases. Licences for importation granted during the year totalled 7,327,501 lb. or £1,854,918 by value as compared with 6,085,530 lb. and £1,500,377 in 1935. The increase is to be attributed partly to the improvement in the colour using industries and partly to the continued introduction of new and improved types of dyes by the foreign manufacturers. Applications for licences showed an increase of 3 per cent., totalling 10,390, as against 10,092, in the previous year.

The Export Side

On the export side the British industry continues to make progress, the exports for last year of 6,155 tons or £1,324,779 by value being the highest recorded, although slightly below 1935 figures in value (£1,339,583). Exports for the first nine months of 1937 reached a total of 90,662 cwt. of dyes and 16,644 cwt. intermediates or £1,054,552 and £78,569 by value, respectively, indicating that on the full year the 1936 figures are likely to be surpassed.

Accurate comparison with other countries is not easy, in the absence of official statistics for Germany, which is still the leading producer. Estimates place the output of Germany at 76,000 metric tons in 1934, as compared with 66,000 in 1933, and it is believed that this figure was surpassed in 1935 and 1936. A substantial part of the German output is exported, chiefly to China and India, and Germany also supplies about half the imports into the United States. German exports in 1936 were 33,743 metric tons, as against 33,933 in 1935, and 33,593 in 1934, figures which suggest that German producers are not sharing in the increased world demand for dyes.

The output of synthetic dyes in the United States reached the record level of 54,100 metric tons in 1936, as against 46,333 tons in 1934, and the previous record in 1929 of 50,645 tons. Exports in 1936 totalled 17,400,000 lb., as against imports of 3,769,000 lb. Official reports for Russia are lacking, but it is believed that Russia has now attained third place in the list of world producers with an output of over 25,000 metric tons in 1935, which was probably increased by 15 to 35 per cent. in 1936 if the planned output was attained, a figure which would enable her to displace Great Britain with her output of 27,330 metric tons.

The Japanese output in 1936 is estimated at 19,065 tons, as against 19,080 tons in 1935 and her military adventures have apparently given a sharp check to the rapid expansion which has characterised the Japanese dyestuffs industry in the last few years. The production in France in 1936 is estimated at 12,210 tons as against 10,480 tons in 1935 and in Switzerland at 7,503 tons in 1936, as against 6,681 tons in 1935.

Co-operation between Manufacturer and User

A feature of the past few years in the British dyestuffs industry has been the steady growth of co-operation between those concerned with the manufacture and the use of dyestuffs. Such co-operation has, of course, been a feature of the development of the industry under the machinery provided by the Dyestuffs Act, such as the Dyestuffs Industry Development Committee. Besides this, the Committee's efforts have led to the manufacture in this country for the first time during the year of a number of dyes which had previously been imported in fairly substantial quantities, and the volume of imports thereby displaced amounted to nearly 500,000 lb.

Co-operation also finds expression in a number of other directions such as the work of the British Colour Council in reducing the multiplicity of shades and securing the acceptance of standard fashion shades. A Dictionary of Colour Standards in both silk and wool has been issued and the Council are about to issue co-ordinated colour cards, making it easier for distributors to ensure that their shades in one department are co-ordinated with shades in another department. This question was also the subject of a symposium arranged by the Society of Dyers and Colourists in Manchester in November, 1936. Similarly, the efforts of the Society of Dyers and Colourists to promote the adoption of international standards in connection with tests for fastness to light represent another field in which user and maker are equally concerned. A further example of such co-operation is to be seen in the Joint Standing Committee on Alleged Dermatitis. This Committee includes representatives of wholesale distributors, retail stores, drapers, outfitters and others interested in the sale of textile goods, as well as furriers, dyers and dye makers and its objects are to investigate all cases of alleged dermatitis stated to be contracted through the wearing of apparel and to resist unjustified claims.

That the possibilities in this direction are far from being

exhausted were indicated in a stimulating address by Mr. C. J. T. Cronshaw to the Manchester Section of the Society of Dyers and Colourists in January. Mr. Cronshaw referred pointedly to the dearth of really good and up to date textbooks. The only noteworthy addition to the literature of the industry during the year is Mr. K. H. Saunders' "The Aromatic Diazo Compounds and their Technical Applications," although it should be noted that workers in the industry are contributing freely to the new edition of Thorpe's Dictionary of Applied Chemistry which is now being published.

British Contributions to the Literature

It is, of course, difficult to disentangle the literature on dyestuffs intermediates from that of organic chemistry generally and perusal of the Journal of the Chemical Society, the Berichte or the Annalen quickly brings to light work which has been assisted in some way or other by such firms as Imperial Chemical Industries, Ltd., or the I.G. Farbenindustrie A.G. The Society of Dyers and Colourists does, however, deserve special mention for the high standard of papers which have appeared in its Journal during the year. Such papers as Ellis Clayton's "Identification of Dyes in Textile Fibres," F. L. Goodall on "The Theory of Wool Dyeing," and on "The Fastness of Wool Dyeings to Wet Treatments," or Professor F. M. Rowe and K. A. J. Chamberlain on "the Fading of Dyeings on Cellulose Acetate Rayon: the action of Burnt Gas Fumes (oxides of nitrogen in the atmosphere) on Cellulose Acetate Rayon Dyes," mark it out in this country as the medium "par excellence" in which important contributions to new knowledge in the industry are normally made. It is indeed a compliment to the Society that Professor H. E. Fierz-David and M. Matter should select its journal for the publication of their investigation of the constitution of azo and anthraquinone dyes containing the cyanuric ring, which in recent years has been the subject of so many patent specifications.

If, however, the British industry makes comparatively few contributions to the published literature there has been no slackening of its research activity. The outstanding achievement of the previous year, Monastral Fast Blue BS, has now been followed by a further advance in Monastral Fast Blue CS, available in both paste and powder forms, which is appreciably greener in shade than Monastral Fast Blue BS and possesses great brilliancy of shade and outstanding fastness properties. A soluble form of Monastral Fast Blue BS has also been introduced in Monosol Fast Blue 2GS, while a soluble brand for colouring paper has been placed on the market under the name Durazol Fast Paper Blue 10GS. Additions to most of the ranges of dyestuffs such as the Caledon colours, the Soledons, Monolite colours, and Chlorazol colours have been made during the year as well as a brand of Methylene Blue BP, conforming to British Pharmacœpia requirements. A feature of the year has been the introduction by Imperial Chemical Industries, Ltd., of an entirely new range of acid wool colours which much surpass in all round fastness properties any acid colours previously marketed by this firm. The first number of this series, Carbolan Blue B3, possesses excellent affinity for wool from a neutral or slightly acid bath and can be applied to loose wool or slubbing in circulating machines or in the open beck.

New Acetate Rayon Dyes

In the field of acetate rayon dyes the British makers continue to develop new and improved products and the new range of Solacet colours introduced last year has been further extended by Solacet Fast Yellow CS and Solacet Brilliant Blue BS. Williams (Hounslow), Ltd., who celebrated the diamond jubilee of the firm during the year, have also extended their range with Resorcin Brown FM, Golden Brown Y, Crispin Brown 3R and Acid Leather Brown ER, as well as introducing a new range of Dermatol dyes for leather which combine satisfactory fastness to light with exceptional penetrating and level dyeing properties. An illustrated brochure issued during the year traces the history of the firm back to its founder, C. H. Greville Williams, the discoverer of the first cyanine dye. Like the Clayton Aniline Co., Williams Brothers are considerably extending their works. L. B. Holliday and Co., Ltd., continue to increase their production of dyes and intermediates, their activities during the year being principally directed to the manufacture of the faster types of colours and in Paradone Yellow 5GK and CC they have marketed two vat dyes formerly imported in considerable amounts.

As already indicated the continental manufacturers have made numerous additions to their own standard ranges such as the Chlorantine, Indanthrene, Celliton, Rapidogens, Ciba and others, the introductions of the I.G. Farbenindustrie A.G., as in former years, representing by far the bulk of the novelties. The growing interest in staple fibre has already attracted the attention of the dye makers and I.C.I. have already introduced a range of Viscrome colours specially designed for dyeing solid shades on wool and viscose staple fibre, either as loose fibres or by a one-bath chrome process. No account of the British industry would, however, be complete without reference to the new finishing agent introduced during the year in Velan PF, which has already been described as an epoch making discovery by the managing director of the Bleachers' Association. Treatment with Velan PF confers water repellency as well as a soft finish and satisfactory resistance to washing and dry-cleaning.

Review of the Literature

It is impossible in the brief space at one's disposal to deal adequately with the technical literature of the industry, which is now far from being confined to aromatic chemistry and ranges over the whole field of organic chemistry including the aliphatic compounds. Such studies as those of K. Lauer on the influence of solvents on the course of chemical reactions such as the sulphonation of anthraquinone (*Ber.*, 1937, *70*, 333) or halogenation, nitration and sulphonation generally (*ibid.*, 1936, *69*, 2,619) or the nitration of nitrobenzene (*J. pr. Chem.*, 1937, *148*, 287) have an obvious bearing on the technique of the industry. Fluorine derivatives continue to receive attention, and the preparation of a number of simple fluoro derivatives of the benzene series has been described by E. V. Zappi (*Bull. Soc. Chim.*, 1937 (V), *4*, 1,936), while J. van Braun's study of amination with anhydrous ammonia (*Ber.*, 1937, *70*, 979), E. V. Starkey's utilisation of the decomposition of the diazonium borofluorides with sodium nitrite in presence of copper to prepare inaccessible nitro comounds (*J. Amer. Chem. Soc.*, 1937, *59*, 1,479), G. Locke and E. Bayer's use of sodium stannite as a reducing agent (*Ber.*, 1936, *69*, 2,666) and C. W. Deane's study of the ring closure of *o*-benzylbenzoic acid in oleum and sulphonic acid (*J. Amer. Chem. Soc.*, 1937, *59*, 249) deserve mention. One of the most important papers of the year, however, comes from the I.G. Farbenindustrie A.G. laboratories (*Annalen*, 1937, *531*, 1) in which H. Vollmann, H. Becker, M. Corell and H. Streed describe the preparation of a large number of pyrene derivatives of all types.

With regard to the literature on dyestuffs themselves several papers during the year dealt with the colour and constitution of azo dyes, among which may be mentioned those of A. Rollet (*Monatsh.*, 1937, *70*, 425). H. H. Hodgson and P. F. Holt dealt with the constitution and affinity for cotton of disazo dyes derived from substituted diaminodiphenyls (*J. Soc. Dyers Col.*, 1937, *53*, 175) and H. Goldstein and M. Stranli have investigated the azo dyes derived from 1 : 3-naphthylenediamine. H. E. Fierz-David and E. Mannhart have investigated the azo derivatives of 2-methyl-*a*-naphthylamine-4-sulphonic acid. K. Brass has continued his investigation of substantivity and constitution, a study of the comparative substantivity of J-acid, Gamma-acid and their ureas leading him to regard substantivity as the resultant of several constitutional factors (*J. pr. Chem.*, 1937, *148*, 35). P. Pfeiffer's investigation on the internal salts of azo compounds has some bearing on the structure and properties of

the chromium and copper dyes now in use (*J. pr. Chem.*, 1937, *149*, 217). A paper bearing on the old synthesis of indigo from *o*-nitrobenzaldehyde appeared in the *Bulletin de la Societe Chimique* (1937, *4* (V), 1,673), in which I. Tanasescu and A. Bacin describe the preparation of a number of additive compounds from *o*-nitrobenzaldehyde and substituted acetophenones which all yield indigo in dilute alcohol in presence of alkali. P. Ruggli and H. Reichwein have also contributed a note on the preparation of indigo from ortho substituted acetophenones, obtaining yields up to 73 per cent. by warming *o*-acetylamino bromoacetophenones with methyl alcoholic potassium hydroxide and aerating the melt (*Helv. Chim. Acta.*, 1937, *20*, 913). Waldmann has obtained a hitherto unknown isatin 5- and 6-carboxylic acids from *p*- and aminobenzoic acids (*J. pr. Chem.*, 1937, *147*, 338). The benzoyl derivatives of indigo continue to receive attention and in a further paper by H. de Diesbach and E. Meser (*Helv. Chim. Acta.*, 1937, *20*, 132) the formulæ previously suggested for Ciba Yellow and its dihydrate and mono- and dimethyl derivatives have been confirmed, although an attempt at synthesis failed. Mention must be made of an exceptionally interesting survey of the constitution and application of the indigosols by Dr. Barder, one of their original discoverers, while the interest shown in the bactericidal or antiseptic properties of azo dyes is reflected in several papers on the immunising properties which have appeared during the year, among which may be cited those by H. E. Fierz-David and his colleagues (*Helv. Chim. Acta.*, 1937, *20*, 16, 1,059). The literature of phthalocyanines steadily grows and in addition to J. M. Robertson's and I. Woodward's quantitative determination of the structure of nickel phthalocyanine by X-ray methods, reference should be made to J. H. Helberger's preparation of a green phthalocyanine pigment which contains copper, but no halogen, by heating *o*-chloroacetophenone or *o*-bromoacetophenone with cuprous cyanide in quinoline (*Annalen*, 1937, *529*, 205). The same worker subsequently showed that *o*-cyanoacetophenone is an intermediate step in the synthesis of copper tetrabenzoazaporphin from *o*-halogenoacetophenones and cuprous cyanide (*ibid.*, 1937, *531*, 279).

Review of Patent Specifications

Turning to the patent field, the I. G. Farbenindustrie A.G. have obtained blue to green phthalocyanine pigments by heating dintriles such as phthalonitriles with acid amides like formamide (B.P. 457,526). Increased yields are obtained by modifying the conditions (B.P. 458,754). I.C.I. have also described an alternative route for copper, iron and nickel phthalocyanines by heating ammonium phthalate with copper, iron or nickel or tin salts and an aminosulphonic acid (B.P. 457,786). They have also claimed the manufacture of chlorinated or brominated phthalocyanines containing at least eight halogen atoms (B.P. 461,268). The I.G. also describe a process for converting the alkali metal salts of sulphonated phthalocyanines into lakes (B.P. 457,796) and, in a further specification, claim the use of a diluent such as nitrobenzene or trichlorobenzene in the preparation of the phthalocyanine (B.P. 459,780).

A Dupont specification (B.P. 456,774) relates to the manufacture of highly dispersed powders of the Fanal type of pigments and the I.G. have a patent for diaminotriphenylmethane dyes for colouring vegetables (B.P. 462,170), while the Geigy Co., obtain insoluble blue to black induline dyes of the nigrosin type, of increased solubility in alcohol, by using alkoxyanilines in place of the usual aniline (B.P. 467,937). In the intermediates field a number of patents for 2 : 6-dimethylnaphthalene sulphonic acid and similar derivatives have appeared as well as beta trifluorotoluene sulphonic acid, 4-hydroxyl-3-alkoxybenzaldehydes, aromatic acid chlorides such as benzoyl chlorides, 1 : 2 : 3 : 4-tetrahydroquinoline derivatives and β-naphthol dicarboxylic acid.

A number of specifications relate to pyrene derivatives and the I.G. have claimed the manufacture of bromopyrene.

In the azo field *o*- and *p*-aminoalkylsulphones (S.C.I., Basle, B.P. 457,679, 457,637) have been claimed as diazo components for new dyes for wool. Kuhlmann obtain a bright greenish yellow milling wool dye by coupling dianisidine disulphonic acid with acetoacetanilide (B.P. 456,957). Aminoarylsulphonyl fluorides have also been claimed as disazo components. (I.G B.P. 460,224), and also *p*-aminobenzene-2 sulphonamides (S.C.I. B.P. 465,955), while acid wool dyes containing metal are obtained by treating with chromium, parent dyes from an *o*-aminophenol and a naphthylamine sulphonic acid (S.C.I., B.P. 466,189), giving violet to greenish shades. Secondary disazo dyes with a nuclear alkyl group containing 10 to 20 carbon atoms are used by I.C.I. to obtain violet shades on wool (B.P. 469,318). Brown acid dyes of good fastness are obtained by coupling an aniline derivative with a long chain alkyl substituent of 8 to 20 carbon atoms such as *p*-dodecylaniline with aminonaphthol sulphonic acids (B.P. 462,176). Orange to violet shades are obtained by I.C.I. by coupling an amine devoid of long chain residues with a naphthol di- or trisulphonic acid and a 1-sulphoaryl pyrazolone (B.P. 465,957). Similar dyes are obtained with, *e.g.*, dodecyl *p*-aminobenzoate (B.P. 466,127). Other specifications relate to trisazo and polyazo dyes giving brown or black shades on leather (I.G., B.P. 455,229, 456,764). 4 : 4′-diaminodiphenylamine being a frequently used component (*e.g.*, B.P. 459,441, I.G.).

New Patents for Ice Colours

New patents for ice colours continue to appear, the I.G. claiming the use of amides of bases of the Fast Blue BB type (B.P. 457,825), as well as aminoazobenzene derivatives (B.P. 458,370), the latter type of base being also claimed by the Society of Chemical Industry, Basle (B.P. 457,047). N-alkyl-4-aminonaphthasultones have been claimed for blue shades (B.P. 463,040) and 3-aminoindoles for brown to green shades (B.P. 462,535).

Insoluble dyes for acetate rayon have been obtained by using *p*-aminophenylalkylsulphones (B.P. 456,343) or amino aromatic carboxylic esters, such as ethyl 3-nitro-4-aminobenzoate as diazo components (B.P. 457,036). Yellow dyes for acetate rayon very fast to light are obtained by the I.G. by coupling a nitroamine and 5 : 6-dihydro-1 : 3-dihydroxybenzene (B.P. 461,765).

I.C.I. obtain violet to blue dyes for acetate rayon giving shades of good fastness and dischargeability by coupling 2 : 4 : 6-trinitroanilines with the sulphuric esters of N-alkyl or N-alkyl-N-hydroxyalkyl-*m*-toluidines (B.P. 457,787), soluble dyes for acetate rayon are obtained by I.C.I. by coupling a *p*-aminoaryl hydroxyalkyl ether sulphuric ester with *p*-cresol (B.P. 466,799).

New substantive dyes for cotton have been obtained by the Society of Chemical Industry (Basle) using benzoylaminobenzoyl derivatives of J-acid or H-acid (B.P. 462,913) and a number of specifications cover copper compounds of polyazo dyes (B.P. 465,902, 464,827, 462,675). I.C.I. use the copper derivatives of such dyes as those obtained by coupling anthranilic acid or 4-nitro-*o*-aminophenol with acetylaminophenyl urea of J-acid (B.P. 462,690) and N-substituted 2 : 7-aminonaphthols are claimed by the I.G. as components of chrome wool dyes (B.P. 459,949).

In the field of sulphur colours, level dyeing blue dyes of good fastness have been obtained by the I.G. by sulphurising leuco indophenols obtained, for example, from N-methyl N-hydroxyethylaniline or N-hydroxyethyldiphenylamine (F.P. 808,972).

In the indigoid field the Society of Chemical Industry, Basle, claimed the halogenation of indigo alizarins, mainly with sulphuryl chloride, to give bluish green dyes of good shades in artificial light (B.P. 460,627). Thioindoxyls obtained from aminopyrene-*o*-sulphonic acid are also claimed for the manufacture of thioindigoid dyes (B.P. 459,891).

In the anthraquinone field, the I.G. have described the preparation of blue to bluish green dyes of improved fastness to acids by condensing a 4-bromo-1-aminoanthraquinone-2-

sulphonic acid with 1 mol. of a diaminodiphenylmethane or diaminotriphenylmethane (Anm. J. 53,265, IVa/22b). Blue shades on wool, fast to milling and severe washing, are obtained by I.C.I. with the 1-hydroxyamino, methylamino 4-carboalkoxyanilinoanthraquinone sulphonic acids in which the alkyl group contains 8 to 15 carbon atoms (B.P. 469,449).

Blue dyes for acetate rayon have been obtained by condensing mixtures of 1 : 4-diamino or 1-amino-4-hydroxy or alkoxyanthraquinones and leuco derivatives such as leucoquinizarin, with primary alkyl aralkyl or cycloalkyl amines (Anm. J. 53,171, IVa/22b) or by condensing 4-halogeno-1-amine anthraquinone-2-sulphonic acids with primary arylamines substituted with a hydroxy alkylsulphamido group (F.P. 807,532). I.C.I. use alkoxybenzanthrones, in which the alkoxy group contains 2 to 5 carbon atoms, to dye acetate rayon (B.P. 466,607).

British Celanese, Ltd., claim the amino or alkylaminoanthraquinones, obtained by replacing one or both hydroxyl groups in a 4 : 4-dihydroxyanthraquinone with ammonia or amines in presence of a heavy metallic compound (B.P. 460,440), and also the use of solutions of dyes in homogeneous liquids containing a carboxylic ester, b.p. below 130°, to dye acetate rayon (B.P. 460,575).

Bluish green, olive, brown and grey vat dyes of excellent fastness are obtained by the I.G. by condensing 1′(N) : 2′-pyridino-(2)-anthraquinones, with a replaceable substituent in the 6-position, with cyclic amines or pyridinoanthraquinones, with an amino group in position 6, with halogen derivatives (B.P. 458,099).

Dyes for oils, varnishes, candles, etc., are obtained by mixing the dye, *e.g.*, 1 : 4-diaminoanthraquinone, with chlorinated diphenyls containing more than 40 per cent. of chlorine (B.P. 459,797, I.G.). Black dyes of excellent fastness to kier boiling and light are obtained by mixing dyes of the dibenzanthrone or isodibenzanthrone series with the colours obtained by alkaline fusion of 1-(3-benzanthronylamino) 4- and 5-, or 8-acylaminoanthraquinones (F.P. 808,122, I.G.).

Among interesting I.C.I. specifications should also be mentioned those for the conversion of dyes soluble in water into modifications soluble in organic solvents by conversion to quaternary ammonium, or phosphonium, or ternary sulphonium salts, *e.g.*, by treatment with cetyl pyridinium bromide (F.P. 867,052) and of the use of vat dyes for dyeing cellulose, viscose or wool from alkaline vat in presence of a ternary sulphonium salt, such as *p*-lauramidophenyldimethylsulphonium methosulphate (B.P. 464,110).

Oils and Fats: A Review of 1937

By
C. D. BUTLER, M.Sc.

WHATEVER may be the economic situation which determines the profit-earning capacity of any new technical development, no one, surveying the progress of the last twelve months, can refrain from commenting upon the ceaseless activity of research and control chemists in their continual presentation for wider application of endless new variations in the utilisation of raw material and in its refining and testing.

Particularly is this so in the field of fats, both liquid and solid, waxes and their derivatives. Although the weight of capital invested in the industries which manufacture edible fats, soaps, paint, leather, and lubricants may seem to give standard procedures enormous inertia, yet examination shows that in works laboratories as well as in research institutions suggestions for the modification of these standard procedures are all the while being thrown up and, in varying degrees, adopted.

It is true that recent years have not shown a major advance in the fats field comparable with, say, the production of polymer gasoline in the petroleum industry. But nevertheless the cumulative progress in development will be apparent if we compare the products of the above-mentioned industries to-day with those which they were turning out in 1920.

As might be expected, one of the influences directing enquiry has been that of the urge towards regional self-sufficiency. This has led to two, at least, main streams of investigation. One has been the production from fatty materials of other substances in which that region is lacking. One of the most interesting of these is the persistent attempt to obtain motor fuels and lubricants from fatty materials instead of from crude petroleum. The restricted producing areas for the latter make any effective substitute source-material of the utmost strategic and economic importance. Yields around fifteen per cent. of a gasoline grade are reported for a French cracking of copra, peanut and cottonseed oils. Liquid phase cracking of rape oil has been conducted elsewhere, and the conditions of maximum yield established. In China also work of previous years has been continued in the cracking of cottonseed.

The production of synthetic lubricants has possibly an even greater value since, unlike the percentage of motor fuel, the quantity of lubricating fraction to be extracted from a petroleum crude is much more strictly limited. The polymerisation of fatty material with a tin chloride catalyst has provided a polymer of value as a lubricant. Electrical polymerisation has also been investigated with promising results.

A report from another quarter suggests a use for waste fat in the preparation of a weed-killer by the preparation of a complex mercurated compound which appears to be efficacious. Waxes of certain types are also at a premium and suggested substitutes have been produced by the hydrogenation and subsequent polymerisation of castor oil.

Again, considerations of availability may make it desirable to substitute, perhaps after treatment or with the assistance of a blending agent, a cheaper or more plentiful material for the previous rarer or more expensive components. Fish oil, for instance, continues to receive much attention. In the past partial hardening alone has not sufficed to eliminate the possibility of a recrudescence of unpleasant odour. Newer methods are, however, now making it possible to use fish oil in soaps, though its incorporation in paint oils is still limited not only by its dried film characteristics, but also by the presence in it of saturated constituents whose removal is wasteful of the more valuable portions.

Electrically polymerised sunflower oil has been advanced as a good soap fat, the reduction in iodine value following polymerisation giving a harder soap. Subsequent hydrogenation of polymerised and oxidised sunflower oil in the U.S.S.R. has enabled that relatively abundant oil to be used in greater proportion in soap. Similarly treated oil has also been found to be of an edible quality. A further edible material has been produced by hydrogenation of cottonseed oil in the presence of glycerol and a basic catalyst. In the U.S.A. cottonseed oil is being incorporated to a larger extent in margarine and was last year the largest single constituent in American margarine oils. Sulphonated sunflower oil has been proved satisfactory for leather treatment. In particular it appears to confer a good resistance to gas penetration when used in masks.

The utilisation of by-product waste is always of interest and it has been shown that up to ten per cent. of castor seed cake may be incorporated in hen feed without toxic effects. Italian work has proved that cows can be fed with between fifteen and twenty per cent. of olive pulp residue without loss of food value or appetite. Another by-product, pine oil, has been used as a good substitute for more expensive fats in soap

manufacture. Twenty per cent. of it can be used in the fat charge for a bar soap of good detergent value.

Woolwax has been used as the basis of a paint dryer. After saponification with excess alkali it is neutralised with naphthenic acid and precipitated with a heavy metal salt. For varnish manufacture a substitute gum has been prepared by the esterification of amber and in blending with this, as well as with more normal varnish mixtures, oiticica oil is showing itself to be a satisfactory substitute for wood oil.

Fatty Materials from Non-Fatty Substances

The second effect of the desire for 'self-sufficiency' has been to stimulate the attempt to produce fatty materials from non-fatty substances or else to find effective non-fatty substances to replace a more valuable fat. An example of the latter comes from Germany where the lignin-sulphonic acids in waste sulphite liquors from the treatment of cellulose are used instead of fatty acids in the manufacture of soaps of good detergent quality. Other substitutes have been obtained from paraffins and aliphatic alcohols condensed with di- and tri-glycol ethers and then given an acid treatment. It should be noted that Uhl asserts that at high temperatures normal soaps are preferable to the synthetic ones.

Oxidation of paraffin wax has been carried out in Germany for the production of fatty acids. Careful experiment will show to what extent and for what purposes these products can replace natural fats.

Paint materials are also being produced from kerosine by the action of aluminium chloride and also from the residues of redistillation of Gray process polymers. The reduction of the percentage of linseed oil needed in a paint by the use of non-absorbent solid ingredients is also being studied in Germany. The whole problem, of which paint chemists are well aware, in judging whether such newer or the older synthetic ingredients are satisfactory depends to a large extent on the purpose to which the paint is to be put. Both soya oil and our old friend bitumen have received further support during this year. It is of incidental interest to note that in Germany soya is being extracted almost exclusively by solvent methods.

The year has also seen a rapid increase in the output of hydrogenated oils in the U.S.S.R. The formate and other salts of nickel appear to be the catalysts in use.

Another direction of investigation lies in the elimination of what may be broadly termed "customers' complaints." These may be due to new methods of utilising the finished products which show up some inherent defect in them or it may be that some substitute component is not standing up to working conditions. Or it may arise from an attempt to deal with recognised deterioration.

Frying oil, for instance, degrades on continued reheating and recent work has shown that hydrogenated oil such as cottonseed may not be superior to the untreated oil. Nor does the use of stand train oil in varnishes appear to pass without comment and complaint. In the actual production of refined oils themselves the removal of undesired constituents by the process of steam distillation under vacuum is calling for care in the design of non-corrosive equipment.

Leather of the lighter grades is at times liable to "spue," a patchy discoloration on the glaze, and leather chemists have given more attention this year to its cause and removal. The defect has been shown to be due to fatty acid crystals which are caused by an insufficient degreasing of the skins. A mould inside the leather has also been suggested as a contributory cause. The soaps of iron, chromium and aluminium have been found in the spue, and it has been proposed that a solvent degreasing may eliminate the source of the trouble. A patent along these lines has been taken out in which the solvent is mixed with an adsorbent substance. The cracking of shoe leather after wearing has been investigated by an American chemist who, with some degree of heroism, has extracted the soluble perspiration content of well-worn socks and found that it contains substances which are harmful to the wearer's shoe leather.

Rancidity continues to engage the close attention of chemists concerned with, in particular, edible fats. It is established that the formation of peroxides and the increase in rancidity in a fat are not necessarily closely correlated under all circumstances. The peroxide content of cottonseed oil kept in the dark may increase without rancidity to a figure well in excess of that of already rancid oil which has been kept in the light. None the less anti-oxidants such as maize and oat flour have been shown to prevent the onset of rancidity and their use is advised for the dusting of fried chips, fish and nuts. In the case of bacon and pork, bacterial or enzyme action is noted as a partial cause of rancidification. The Stamm test has received criticism in this connection, and it is held that the older Kreis test is of wider validity. With several fats the presence of non-oily matter has been shown to assist rancidity and its removal requires careful attention. The prevention of fat bloom on chocolate by the incorporation of blown cocoa butter is of interest as is also the effectiveness of the same material in inhibition of stearine deposition from olive oil.

Coming to the more analytical side we have seen during the year further devising of new tests and the criticism of older ones. These may be for the detection of adulterants or for the closer control of specifications.

Among the former are new tests for arachis and tea oils in olive and almond, a rapid test for animal oil in a vegetable oil, hardened or natural, and a suggested means of estimating, by double decomposition, the triethanolamine content of a soap. The disturbing effect of an emulsifier such as Tylose SAP in a soap analysis may be obviated by a method suggested by Knippe. Standard tests have also been criticised. Those for the estimation of unsaturation, in particular, have received attention. The Iodine Value for a fat occasionally shows wide variations when estimated by different methods. The Rosenmund-Kulnhenn method seems to be gaining greater support from both paint and leather chemists. The hexabromide determination has been speeded up by Rossman, who does not recover the fatty acids *in toto*, but brominates one portion of their solution while evaporating an equal volume of the solution for weighing. An allowance is also made for the solubility of the hexabromides in ether by doing a parallel estimation with only half the volume of the fatty acid solution.

Estimation by Retractive Index Methods

The estimation of fat in seeds and water in oil have both been calculated by refractive index methods. The fat in Turkey Red oil has also been similarly estimated. Fatty material is dissolved in brom-naphthalene in solvent extraction and the change in refractive index of the solvent noted. In the case of water, glycerol is the extracting solvent, and Zaitschenko gives a formula for the refractive index of glycerol diluted with water and suggests a standard procedure for the test. Errors in the fat content estimation of leather have been discussed, and those arising from oxidation during drying eliminated by a new technique. Leather chemists are also reconsidering their standard tests for sulphonated oils, while tests such as the Bellier and Baudouin are the subject of reinvestigation by the A.O.C.S.

A new solvent, ethylene glycol mono-ethyl ether is proposed for general use in saponification reflux. Its higher boiling point—134° C—reduces the time, even for such recalcitrant materials as wool wax and carnauba, to about fifteen minutes for complete saponification. The KOH is stated to be as soluble in this solvent as in the more usual ethyl alcohol.

Closely allied to the revision of testing methods is the revision of standard figures for both common and hitherto little used fats. Some of those till now taken as correct may, with improved tests, be shown to be either out of date or actually in error. Among the materials thus tested one notes Empire tung, kapok, Algerian olive, Japanese tung, perilla, acorn, passion fruit, esparto.

Certain pieces of fundamental research are of outstanding

(*Continued on page* 538.)

A. O. Bentley.

Progress in Synthetic Drugs and Pharmaceuticals

By

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and

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Dr. H. S. Cox.

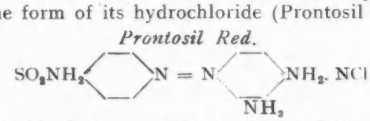
THE introduction of a new curative agent must always be followed by a period of trial and extended clinical experience, and the year has been marked more by the numerous and often conflicting reports as to the value of recently introduced synthetic drugs than by the announcement of new ones. It should not be thought that progress in the synthesis of chemotherapeutic agents has not been made: the contrary is the case, but it happens that only a few new remedies have been marketed during the year.

Streptocidal Agents

The attention of many investigators has been directed towards the discovery of chemical substances capable of destroying streptococci in a manner comparable to the effect of the arsphenamines on spirochætes. The parenteral injection of dyes known to possess effective bactericidal action *in vitro* was found to have only a local effect upon such organisms with which they came into direct contact in the body. The various acridine derivatives are examples of the type of compounds the action of which is more disinfectant than therapeutic.

It was in 1935 that Domagk described the effect of the administration of the red azo-dye, 4-sulphonamido-2′:4′-diaminobenzene in protecting mice against hæmolytic streptococcal infection and this substance was subsequently marketed in the form of its hydrochloride (Prontosil Red).

Prontosil Red.

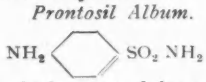


Hydrochloride of 4-sulphonamido-2′:4′-diamino- -azobenzene.

It was later shown (*Lancet*, 1937, *23*, 1) that this compound was changed in the body to *p*-aminobenzenesulphonamide and that it appeared to be this substance which was responsible for the bactericidal action. Moreover, *p* aminobenzenesulphonamide is a white, crystalline substance which, if equally effective, has obvious advantages over a red dye. It was found that this substance had a bacteristatic and bactericidal action and that when administered to man or animal their blood became bactericidal to hæmolytic streptococci.

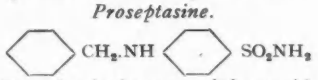
Under the name of Prontosil Album, *p*-aminobenzenesulphonamide was introduced for use in place of the dye, as was also Proseptasine which is claimed to be less toxic and which is *p*-benzylaminobenzenesulphonamide.

Prontosil Album.



p-Aminobenzenesulphonamide.

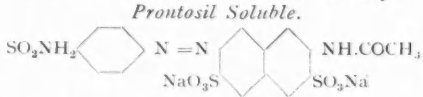
Proseptasine.



p-Benzylaminobenzenesulphonamide.

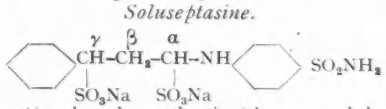
For parenteral administration a water soluble form of the original dye was introduced under the name of Prontosil Soluble and has the formula given below. Another water soluble, white, crystalline substance for parenteral administration was marketed under the name of Soluseptasine.

Prontosil Soluble.



Disodium Salt of 4′-sulphamidophenyl-2-azo-7-actylamino-1-hydroxynaphthalene-3:6-disulphonic acid.

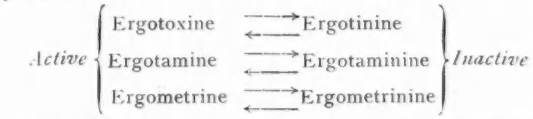
Soluseptasine.



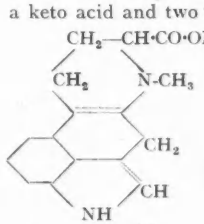
Disodium-*p*(γ-phenylpropylamino)-benzenesulphonamide-γ-disulphonate.

Ergot Alkaloids

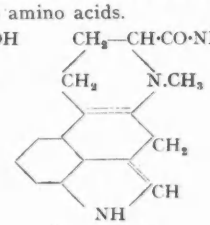
At long last it may be said that the chemistry of the alkaloids of ergot is understood. The drug is now known to contain four pairs of interconvertible isomerides, the molecular formulæ of which are now well established. The three most important alkaloids and their isomerides are :—



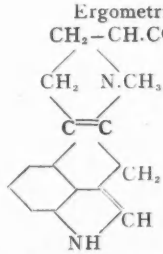
The active alkaloids are lævo-rotatory and crystallise from organic solvents. The inactive alkaloids are dextrorotatory. It is known, as the results of the researches of W. A. Jacobs and his co-workers, that all the ergot alkaloids may be hydrolysed to an indole derivative, lysergic acid. Ergometrine and its isomer yield lysergic acid and hydroxy*iso*propylamine. The other alkaloids yield a number of substances such as ammonia, a keto acid and two amino acids.



lysergic acid.



Ergometrine



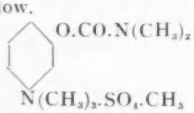
General formula of ergot alkaloids

It is probable that in the near future ergometrine, the most important of all the alkaloids and also the simplest, will be synthesised. The essential difference between the action of ergometrine and that of the other active alkaloids is that the effect of ergometrine is more rapidly produced though less prolonged, but the effect may be prolonged by an initial administration by injection followed by oral dosage.

Prostigmin

Although this cannot be described as a new drug, it having been in use for over a year, an increased knowledge has been obtained of its mode of action. The reproduction of nerve action is due to the release at the nerve endings of some chemical substance. Usually, nerves of the sympathetic system liberate at their endings a substance similar to adrenaline and known as sympathin. Parasympathetic nerves and a few sympathetic nerves releases acetycholine. The alkaloid physostigmine intensifies the effect of acetylcholine because of its property of inhibiting the action of an enzyme, choline esterase, which normally brings about the hydroysis of acetylcholine with liberation of less effective choline. It is thought that the action of physostigmine is due to the fact that the enzyme is used up in bringing about the hydrolysis of the alkaloid.

The instability of solutions of physostigmine and the toxicity of the alkaloid are drawbacks to its use and have led to the introduction of Prostigmin, an analogous substance which has the formula given below.



Dimethylcarbamic ester of 3-hydroxyphenyl-ammonium methylsulphate.

Prostigmin is employed as a stimulant of peristalsis and is also used in a disease known as myasthenia gravis which is characterised by the weakness of certain muscles.

Preparation of Insulin

Various experiments have been carried out by Hagedorn of Copenhagen, a pioneer in insulin therapy, with the object of producing a form in which the effect of insulin could be prolonged and the need for daily injection avoided. He considered the possibility that crystalline insulin as produced by manufacturing processes may be actually a simpler form of the substance than that which exists in the body. He, therefore, searched for some means of preparing the insulin to be injected in an insoluble form from which the active substance would be slowly released after administration.

Protamine insulin consists of insulin combined with protamine, a protein (monoprotamine) found in the testis of the salmon, *Salmo irideus*. A solution of this substance mixed with insulin yields a precipitate at *p*H 7.3, and after injection the precipitate slowly decomposes liberating active insulin into the blood stream. The injection has approximately the same reaction as the blood and, therefore, has the further advantage of causing less pain owing to its lack of acidity compared with ordinary injections of insulin. A particular advantage of this form of insulin is that it may be injected during the evening and thus controls the blood sugar during the night.

Protamine Insulin

A further advance was the discovery by Scott, of Toronto, that crystalline insulin is a compound of zinc, and that when freed from zinc by electro-dialysis the product would no longer combine with protamine. It has been shown previously by Dudley and Rosenheim that a pancreatic protein, spermine, was present with insulin in the early stages of manufacture. Scott has shown that spermine will combine with insulin in the presence of zinc in a manner similar to the combination of protamine with insulin. There are now marketed various brands of protamine insulin (with zinc) in the form of suspensions for use either alone or accompanied by injections of ordinary insulin.

The clinical possibilities of insulin tannate were investigated by Hagedorn, but he discarded it on account of local reaction. Bavin and Broom studied the effect of adding zinc to tannic acid insulin with a view to avoiding local reactions and pain on injection. They have reported that the evidence obtained justifies a clinical trial of tannic acid-insulin-zinc, containing tannic acid-insulin in the ratio of 2 : 1 and 1 mgm. of zinc to each 500 units of insulin. They state that the precipitated tannic acid-insulin-zinc complex is absorbed much more slowly than ordinary insulin, but that the prolongation of its action appears to be due to the fact that tannic acid is a general protein precipitant and that precipitated tissue proteins may form a barrier which still further delays the absorption of the insulin. This view is supported by the fact that the retarding efficiency of tannic acid-zinc increases with the tannic acid-insulin ratio beyond that necessary to form insulin tannate.

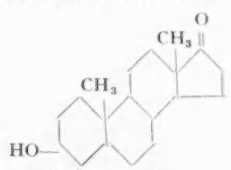
Suprarenal Cortex

The adrenal cortex has been found by Reichstein to yield a number of closely related ketones of the cyclopentanophenanthrene series. A number of suprarenal cortical extracts have been prepared and the effects in cases of Addison's disease have been observed on behalf of the Therapeutic Trials Committee of the Medical Research Council; five of nine patients responded well to the treatment. Typical extracts are Cortin, Cortidyn, Eschatin and Eucortone. In addition to their use in Addison's disease such preparations have been successfully employed in the treatment of shock due to burns, indicating that in such cases either the suprarenal cortex is unable to produce the usual quantity of hormone or that the demand of the body is greater than normal under such circumstances.

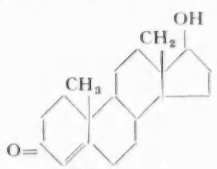
Male Sex Hormones

The recent output of research concerning these hormones has been so great that practical application has not had time to keep abreast. The complexity of the composition of the sex hormones has been demonstrated and in this connection the services of organic chemistry are probably more important than in any other branch of endocrinology.

It has been known for some time that normal male urine contains at least two active substances, androsterone and dehydroandrosterone. Crystalline androsterone was first isolated from this source by Butenandt, in 1931, but the yield from this source and also that of testosterone which was isolated from the testes is extremely small. In 1934 Ruzicka first synthesised androsterone from cholestrol and the so-called synthetic pure male hormones are now more readily available than the same substances from natural sources.



Androsterone



Testosterone

Although these account for most of the Androgenic activity of the testes and urine, it is possible that there exist also other active substances not yet isolated, but our present knowledge places chief importance on androsterone and testosterone. These are colourless crystalline substances, insoluble in water, but soluble in oil. Oral administration has proved relatively ineffective and the usual mode of administration is by intramuscular injection of an oil solution.

Both these substances are secondary alcohols which readily form esters having modified biological activity. It has recently been shown that the most important esters from the therapeutic point of view are those made from simple fatty acids. In 1936 Ruzicka and Wettstein prepared, amongst others, a series of esters from formate to valerate and extensive biological experiments have since shown that the propionic ester is much more active than free testosterone.

(*Continued on page* 537.)

The Manufacture of Paint Products and Lacquers

Review of the Developments and Progress Made

By

H. W. CHATFIELD, B.Sc., A.I.C.

THE progress of recent years has been maintained in 1937, but controlling forces have had some influence upon the direction of activity. The dominating factors which have made their strength felt are the general increase in the price of raw materials, the difficulty of obtaining supplies due to the upsetting influence of wars, and the fact that the persistent demand for finished products has prompted the manufacturer to devote his time to supplying them instead of embarking on fresh work of an investigatory character. It has been shown also that many raw materials have consolidated their positions in the industry. The old and false prediction that cellulose lacquers would oust oil varnishes has been exposed already, but the present year has shown the prediction of the substitution of cellulose lacquers by synthetic resin varnishes to be equally false. There has been an increased tendency to formulate combination lacquers. Materials like chlorinated rubber which were received doubtfully have now established themselves and found useful places when special results are required.

Cellulose Products and Plasticisers

Much progress has been made in cellulose products. There has been a distinct tendency to formulate lacquers for paper to the detriment of the old well-established spirit varnishes. Such lacquers have been either straight cellulose lacquers or emulsions. Centola[1] claims to have stablished nitrocellulose by treating it with methyl or ethyl alcohol. X-ray examinations show that the crystalline structure of the cellulose is unchanged, but it is believed that the alcohols remove sulphates which are a cause of instability. Another method of stabilising nitrocellulose is contained in U.S.P. 2,077,455 which specifies repeated washings to remove free acid and a final treatment with a solution of a nitrite of an alkali or an alkaline earth. Hemp has been nitrated successfully by Parravano and Centola[2] using a mixture of nitric and sulphuric acids. The large amount of non-cellulosic constituents present in the hemp, are removed during nitration and leave large spaces in the micelle which make the removal of nitrating agents more certain. This results in a more stable cellulose nitrate than that obtainable from cotton.

Yellowing of nitrocellulose on exposure to light is caused by the presence of traces of iron or copper salts which may have been present in the original cellulose, in the plant used for nitration, or in the nitrating itself.[3] An examination of the factors affecting the viscosity of nitrocellulose has been done by Lin.[4] Reduction of the viscosity of nitrocellulose before nitration was abandoned, since it was found that the viscosity of the cellulose was independent of that of the nitrated cellulose. The temperature of nitration was important. Nitrocellulose after refluxing at 80° C. for 14 hours with alcoholic alkali showed a considerable decrease in viscosity but some disintegration had occurred also.

New cellulose esters which have attracted some attention are the formate and the acetobutyrate. The tri-formate is prepared by kneading cellulose below 40°C. with a solution of 50-60 parts of zinc chloride in 100 parts of formic acid.[5] Cellulose acetobutyrate is generally more compatible with solvents, plasticisers and resins than cellulose acetate and moulds better.[6] For moisture-resistance it is intermediate between cellulose nitrate and acetate.[7]

Work on other cellulose derivations has continued, but has been concerned chiefly with benzyl and ethyl cellulose.

During the benzylation of cellulose the viscosity of the product increases with temperature of benzylation, but decreases as the concentration of sodium hydroxide increases.[8] Lorand and Georgi[9] believe that the process of benzylation is one in which the reaction commences at the surface of the fibre and then proceeds with each layer in turn. At 60° C. the speed of reaction and the rate of diffusion are similar, but for higher temperatures the speed of reaction is greater than the rate of diffusion.

Legrain[10] found that the viscosity of ethyl cellulose can be reduced by autoclave treatment at 100° C. Of acidic reagents, dilute hydrochloric acid was the most effective but appreciable reductions were possible with oxalic, sulphuric and phosphoric acids. Aqueous alcoholic solutions of potassium hydroxide, ammonia, and triethanolamine, produced reductions of the order of 20 per cent. Salts with alkaline or acidic reactions, and water, all had some effect on the viscosity of ethyl cellulose.

Hydroxyethyl cellulose is prepared by using ethylene oxide and ethylene chlorhydrin. Hydroxyalkyl ethers may be nitrated, benzylated, acetylated, etc., to give valuable lacquer bases.[11]

A successful plasticiser for cellulose esters has been prepared by acetylating the hydroxy groups of glyceryl monolactate to produce glyceryl lactate triacetate.[12] For nitrocellulose films, benzyl butyl phthalate and triphenyl urea have excellent weathering properties.[13] Dodecyl abietate, dodecyl hydroabietate, dodecyl salicylate, and tetradecyl abietate are cited as plasticisers for nitrocellulose in U.S.P. 2,062,450. As a water resisting plasticiser for paper, sorbitol is suggested.[14] The interest in chlorinated diphenyls as plasticisers for nitrocellulose has continued. Andrianov[15] has shown that increased chlorine substitution produces diminished compatibility, but resistance to heat increases with chlorine substitution. For benzyl cellulose, dicresyl monoacetin gives good results but phthalates are unsatisfactory.[16] Oxidised abietic resins are said to improve the durability of nitrocellulose lacquers.

Matt cellulose lacquers may be made by the addition of a solution of orthoboric acid in methyl alcohol.[17]

Driers

Naphthenates have now become commonplace and are used in considerable quantities. This year has seen a persistent interest in cerium naphthenate backed by a steady demand. There are strong indications that this drier will replace the lead salt to an appreciable extent in the future.

Cobalt and manganese linoleates have shorter induction periods than the lead salt.[18] Naphthenates of lead, zinc and calcium are produced direct from the oxides by moistening the latter with a solvent for the naphthenate and allowing the damp oxides to react with naphthenic acid.[19]

A combination drier containing both the acids from lanolin and naphthenic acid is made by fusing them with oxides, hydroxides or certain salts of drying metals. In D.R.P. 636,760 an example states that 750 parts of lanolin fatty acids and 250 parts of naphthenic acids are heated to 100° C. While the temperature is raised to 150° C., 260 parts of litharge are added. D.R.P 636,092 cites the production of similar drying salts by precipitating them from an aqueous solution of mixed sodium salts of naphthenic and wool fat acids by the addition of salts of cobalt, lead, etc.

Metallic salts from the fatty acids of wool fat are made by fusing the acids with the acetates of lead, cobalt, manganese or zinc at 105-160° C. until all the acetic acid has been removed.[20] Lead, cobalt and manganese salts of oil soluble sulphonic acids obtained from petroleum are used as drying salts.[21]

Metallic salts soluble in benzene and useful as driers are made from acids like capryloxyacetic acid according to D.R.P. 632,655.

According to Russ. P. 47,022, neutral zinc resinate may be made by heating 100 parts of rosin and 20 parts of linseed oil at 270-280° C. 12 parts of zinc oxide in 10 parts of linseed oil are then added. Zinc resinate gives more water-resistant varnishes than those made with calcium resinate.[22]

The introduction of a few per cent. of chromium oleate to paints containing titanium dioxide has been shown to have a marked influence in reducing the tendency to chalk on exposure.[23]

Stillingates of all the usual drying metals have been made by Ching-Chien Wu and Yu-Lin Yao by precipitation from sodium stillingate. Cobalt stillingate is the best drier.[24]

O-hydroxycyclohexylammonium stearate is soluble in water and hydrocarbons and is used as an emulsifying agent. It is made by heating stearic acid to 85° C., when *o*-aminocyclohexanol is added. The temperature is maintained at 85° C.[25]

Oils and Varnishes

Uncertainty of supplies with rise in price caused new work on the substitution of wood oil. Oiticica oil has established itself as a good partial substitute. Wood oil substitutes from castor oil are now beginning to appear in bulk quantities, but their value has yet to come under a critical survey. Perilla oil is being used in larger quantities.

Many of the rarer oils have been examined for their suitability as paint or varnish constituents. Grapeseed oil has attracted the attention of Kaufmann and Fiedler.[26] Brambilla and Balbi state that it can replace linseed oil satisfactorily.[27] Stand oils prepared from Iguape walnut oil are claimed to be valuable paint oils.[28] Po-yok oil has been examined further by Rheineck,[29] who has commented on its similarity to oiticica oil. Bonito oil, possessing an iodine value of 209.7 is suggested for use in paint manufacture by Ueno and Matsuda.[30] Although the iodine value of stillingia oil is higher than that of wood oil its drying power is inferior.[31] Shen[32] notes, however, that the oil is better than linseed oil and as good as wood oil when used in paints and varnishes. A semi-drying oil with an iodine value of 141 has been extracted from Grandilla seed.[33] Tomato seed oil has been obtained from the dried seeds by Ovanesian,[34] but it appears to have only slight drying properties. Brambilla and Balbi[27] state that it must be mixed with a large proportion of linseed oil to be of any value in the paint trade. Schuette and Brooks[35] extracted elderberry seeds to obtain an oil of iodine value 162-171.7 which dries slightly better than linseed oil. Processed fish oils are suggested as substitutes for wood oil and linseed oil.[36] Firnagral, which is a mineral drying oil, is proposed as a substitute for linseed oil. It has the advantage of good alkali resistance and low price, but has a very dark colour.[37]

Patents relative to the vacuum distillation of polymerised drying oils are still appearing, *e.g.*, U.S.P. 2,065,728 in which the removal of unpolymerised oil and free fatty acids is effected by a vacuum distillation using a vacuum of the order of the cathodic vacuum. Vacuum distilled stand oils possess many valuable properties including better drying power, low acid values and no tendency to cause precipitation of driers.

Work on the catalytic polymerisation of oils has continued and the results of Van Vlodrop[38] indicate that sulphur dioxide is a valuable catalyst. Hydrochloric acid stimulates hydrolysis.

Research into the deodorisation of wood oil has been conducted by Tchang and Wang.[39] Moisture seems to be the promoter of odour and its effect is accelerated by the action of light and air. Temporary deodorisation was obtained by passing steam, carbon dioxide, or air under reduced pressure through the heated oil.

The "crawling" of perilla oil films can be prevented by the addition of 0.01 per cent. of benzene-azo-benzene-azo-β-naphthol.[40]

The introduction of alkyl esters of abietic acid, *e.g.*, ethyl abietate, to oil varnish is claimed to improve the alkali resistance.

Phenol has been shown to react with the double bonds of pilchard oil to produce ethers. These undergo rearrangement and form substituted phenols which are valuable wood preservatives.[41]

Mono and diglycerides of the fatty acids of linseed and wood oil are suggested as valuable ingredients for varnishes and resins. Monoglycerides are reacted by heating with highly acidic resins, such as rosin or natural gums, to produce low acid value combination products. Diglycerides have been suggested for the production of glyptal resins.

The drying time of ester gum varnishes may be reduced by thirty-three per cent. by the addition of ten per cent. of ethyl cellulose.[42] The drying time of alkyd varnishes depends upon the molecular weight of the alcohol present, the degree of polymerisation and the temperature of formation.[43] Beutel and Kutzelnigg[44] state that the ageing of resin films minimises the effect which water has on them. Resins which obey this theory are rosin, mastic, sandarac and dammar.

Pigments

Lead titanate has attracted a good deal of attention in the past year. It is claimed greatly to improve the durability of paints and varnishes containing it. It is formed by heating together precipitated titanium dioxide and fume litharge. An X-ray diffraction study of its structure has revealed that it is orthorhombic and corresponds with the formula $PbTiO_3$.[45] Nicholson[46] has also studied the product obtained by calcining litharge and titanium dioxide. X-ray study has shown that a compound is formed when the substances are present in equimolecular proportions; excess of either results in a physical mixture of lead titanate and the substance in excess. Products similar to $PbTiO_3$ were obtained by heating hydrous titanium dioxide with either lead nitrate or hydroxide.

Metallic phthalates have been studied by Gardner.[47] Lead phthalate is a transparent pigment which may be ground in varnishes to give improved durability. Titanium phthalate may be used with titanium dioxide to minimise chalking and fading. Mercury and copper phthalates are valuable antifouling pigments.

The composition of commercial zinc chromes has been examined by Brizzolara, Denslow and Rumbel.[48] Analyses correspond with the formula K_2O, $4ZnO$, $4CrO_3.3H_2O$.

An X-ray study of basic lead sulphates by Clark, Mrgudich, and Schieltz[49] has confirmed the existence of $4PbO$, $PbSO_4$ and $2PbO$, $PbSO_4$. There is also a probability that $3PbO$, $PbSO_4$ exists also.

Phthalocyanine derivatives of all common metals were described by Linstead and others.[50] Robertson and Woodward[51] have shown by X-ray analysis that the structure of nickel phthalocyanine is similar to free phthalocyanine. The central nickel atom causes a small inward shift towards itself of the iso-indole nitrogen atoms. B.P.464,673 cites the use of small percentages of orthoboric acid as a catalyst in the production of phthalocyanines. An example states that urea and orthoboric acid are melted and copper chloride and phthalic anhydride added. The resultant mixture is heated to 200° C.

Black titanium pigments of good durability and hiding power are made from rutile and ilmenite by heating in a reducing atmosphere.[52] Pigments giving a mother-of-pearl effect are $BiONO_3.H_2O$ and PbS_2O_3.[53] Magnesium silicofluoride is generally employed in compositions for treating alkaline cement and plaster surfaces before repainting.[54]

Williamson[55] has demonstrated that titanium dioxide darkens in daylight, but storage in absence of light causes the regeneration of the original whiteness. The caking of this pigment may be prevented, according to Canadian Pats. 366,308-9, by precipitating on the dry pigment about 0.25 per cent. of wax or stearin.

Resins (Natural and Synthetic)

The development and evolution of new synthetic resins has continued and the patents appearing are as numerous as ever. The treatment and possibilities of natural gums are receiving more attention.

Gardner[56] has conducted original research on copaiba balsam

as a new raw material, but results do not indicate that it is a valuable acquisition to the existing range.

Esterification of rosin may be accomplished according to Liang[57] by using 12 per cent. of glycerol with zinc oxide or succinic acid as catalysts. The recommended temperature is 280° C. and the process should be conducted in the presence of carbon dioxide for three hours. The melting point and molecular weight of rosin may be raised and the acidity and iodine value reduced by treating a solution of it in petrol with an 81 per cent. solution of aqueous sulphuric acid. The acid is removed and the modified rosin solution is washed.[58]

Abietic acid or abietyl alcohol are hydrogenated in the presence of catalysts to reduce the degree of unsaturation and give products having improved colour and higher melting points.[59] Rosin of improved colour is obtained, according to U.S.P. 2,081,890, by reacting a boron compound with it at 100-225° C. A reaction occurs between the boron compound and the coloured bodies in the rosin to produce a compound which is insoluble in the normal rosin solvents.

The crystalline form of crystals obtained from rosin solutions depends upon the temperature of formation. Crystals similar to those of abietic acid were obtained at 75° C.[60]

Mastication of copal resins to produce the desired solubility has been commercially satisfactory. B.P. 457,637 describes the process whereby copals can be made more soluble in ethyl alcohol. Congo copal is masticated for two hours at 120° F. at a pressure of 90 lbs. per square inch. Water cooling prevents any increase in temperature. Gums thus treated and suggested as shellac substitutes are congo, benguela, manila and pontianac.

Esterification of copals is effected with glycerol in the presence of superheated steam.[61] Superheated steam may be used also during the running process.

Hydrogenation and decarboxylation of congo copal occurs when the copal is subjected to catalytic hydrogenation at 350-400° C. and a pressure of 100 kilograms per square cm. in the presence of a nickel-quartz catalyst. An oil is obtained with very low acid and iodine values and boils chiefly below 200° C.[62]

The durability of varnishes containing natural gums is said to be proportional to the ratio of the alcohol insoluble acids. These are obtained by hydrolising the "run" resin. The former acids have a molecular weight of 900 and the latter a molecular weight of 450 approximately.[63]

An alkyd resin containing shellac is cited in B.P. 468,542 and is made by reacting shellac with a polyhydric alcohol, adding a fatty oil or resin acid and esterifying the whole with a polycarboxylic acid. A drying alkyd resin containing castor oil is made according to U.S.P. 2,074,509, by heating phthalic anhydride, glycerol and castor oil at 260-270° C. for 1½ to 2 hours. Alkyd-phenolic resins which are soluble in oil and which harden on heating are made by condensing a phenol with excess of formaldehyde in the presence of an A stage oil soluble alkyd.[64] Oil soluble phenol-aldehyde resins are made by condensing 2 parts of phenol with 1 part of formaldehyde in the presence of sodium acetate as catalyst, and then heating at 180°-240° C. with 25-35 per cent. of linseed or castor oil.[65]

Bures and Masarek[66] have studied the phenol-formaldehyde condensation. The most effective catalysts are strong acids or alkalis. *m*-Cresol is more reactive than *p*-cresol and commercial phenol is more reactive than pure phenol. The structure of resol[67] which is the product obtained by condensing together 6 molecules of phenol and 5 molecules of formaldehyde with one per cent. of caustic soda is :—

$$\begin{array}{l} H(C_6H_2(OH)CH_2)_m(C_6H_3(OH)CH_2)_nC_6H_4OH. \\ \quad\ | \\ \quad CH_2OH. \end{array}$$

Resol may condense with phenol to form a novolac in presence of one per cent. of hydrochloric acid. Its structure is given as :—

$$\begin{array}{l} H(C_6H_2(OH)CH_2)_m(C_6H_3(OH)CH_2)_nC_6H_4OH \\ \quad\ | \\ \quad CH_2C_6H_4OH \end{array}$$

The condensation of the resol to resite results in the reaction between the C_6H_4OH and CH_2OH groups.

Seebach[68] has isolated *p-p*-dihydroxydiphenylmethane from a reaction between phenol and formaldehyde in the presence of an acid catalyst. A compound of phenol and hexamethylenetetramine was isolated when an alkyline catalyst was present. *o-p*-Dihydroxydiphenylmethane has also been detected. During the formation of urea-formadehyde resins the presence of a catalyst which serves the dual role of catalyst and also combines with excess formaldehyde is suggested in F.P.803,129. Sulphonamides perform these functions. Powdered zinc prevents catalysis. Water soluble urea-formaldehyde resins may be made if the two components are reacted below 35° C. in the presence of methyl alcohol.[69]

A resin containing formaldehyde but soluble in hydrocarbons is made from the reaction product of dicresylpropane and 40 per cent. formaldehyde, by removing water by distillation and heating with drying oils or rosin to 125-135° C.[70] Resins soluble in methylene chloride, aromatic hydrocarbons and cyclohexanone are made by polymerising phenyl vinyl ketone.[71]

Polymeric acrylic acid esters have attracted some attention in the past year. U.S.P. 2,073,619 suggests that the polymerisation proceeds in the presence of a peroxide, which may evolve oxygen, or in the presence of oxygen. Resins can be obtained by reacting carbamic acid esters with aldehydes in the presence of acidic catalysts.[72] A study of the catalytic polymerisation of vinyl acetate was made by Ushakov and Fainshtein.[73] The addition of more catalyst or an increase in temperature gives more extensive polymerisation. With benzoyl peroxide a direct polymerisation produces hard highly polymerised resins, but if the polymerisation occurs in solvents, softer resins are obtained. Pale cumarone resins may be made according to Polish P. 21,423 if the polymerisation of tar oils with sulphuric acid is allowed to proceed in the presence of oxygen inhibitors such as aniline or aniline salts.

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(*Continued on page* 538.)

Recent Developments in Solvents and Plasticisers

By
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A GOOD criterion of the growing importance of the solvent and plasticiser industry is to be found in the statistics for solvent production both at home and abroad. These show that the production of the well-known alcohols, esters and ketones have in almost all cases shown substantial increases; in the case of the U.S.A. increases of as much as 30 per cent. have been recorded. In Great Britain, as in no other country in the world, ethyl alcohol forms the raw material for the bulk of the synthetic solvents, and for the first nine months of 1937 there has been a 27 per cent. increase in production compared with the corresponding period of 1936. Although this increase is due to a large extent to the greatly increased quantities of alcohol being used as motor fuel, there has been a substantial increase of approximately 10 per cent. in the amount of alcohol used as a solvent (industrial methylated spirits), and as a raw material in the manufacture of acetone, acetic acid, ethyl esters, butanol and butyl esters.

Hydrocarbon Raw Materials

One significant fact that has been noticeable recently is the gradual increase in the use of hydrocarbons, such as acetylene, olefines produced during the cracking of petroleum products, and natural gas, as raw materials in the production of the lower aliphatic solvents. This is particularly evident in U.S.A., where some 30,000,000 gallons or 16 per cent. of the total ethyl alcohol produced in 1936 was obtained from ethylene. It is stated that 23 aliphatic alcohols are now produced synthetically in U.S.A. In Russia, also, attempts are being made to build up a synthetic solvent industry based on the use of olefines.

There are two distinct methods known for producing alcohols from olefines; one is a two-stage process using sulphuric acid, and the other a single-stage combination of olefine and steam over a catalyst. In order to produce isopropyl alcohol from propylene with the minimum consumption of sulphuric acid, a process was developed on a large scale some years ago in the U.S.A. in which liquid propylene is emulsified with the acid at a low temperature and the resulting di-isopropyl sulphate hydrolysed by steam. From recent work it appears that a somewhat similar process can also be used in the case of ethylene. If a mixture of olefines is to be treated, it is possible to conduct the reaction under such conditions that the undesirable and more reactive tertiary olefines are destroyed, without affecting the primary or secondary olefines.

Catalytic Hydration

In Russia a great deal of work has recently been published on the catalytic hydration process, using such catalysts as a mixture of nickel and auminium oxides, and the conclusion has been reached that the catalytic method is more economic than the sulphuric acid process. Another suggested catalyst for this reaction is boron tri-fluoride, the use of which was first proposed for a large number of different reactions by the late Dr. Nieuwland. Alcohols produced from olefines have usually to be purified, and one of the more recently suggested methods is by passing the alcohol vapour over a brass catalyst followed by distillation with alkalies, which removes odorous paraffin hydrocarbons.

An interesting comparison of the methods of producing alcohols from molasses, starch, fusel oils, acetylene and olefines was given by Schoen (*Annales de Fermentations*, 1937, *3*, 321).

The projected erection, in Great Britain, of factories for producing large quantities of calcium carbide will give this country a much needed source of home-produced raw material for use in emergencies.

There has been a considerable amount of investigation into the fermentation methods of producing butyl, isopropyl and ethyl alcohols and acetone from carbohydrates in order to trace the course of the reaction and to provide more accurate *p*H control by regulating the type of neutralising agent used during the fermentation. The employment of carbohydrates other than corn starch for this type of fermentation has received much attention, and among the materials investigated have been soya bean starch, the effluent from potato starch factories, molasses and even sulphite-cellulose liquors. One interesting patent dealing with the production of isopropyl and butyl alcohols from molasses describes how the ratio of the alcohols produced can be varied by adjustment of the *p*H at different levels.

The production of methanol still continues to expand, especially in the U.S.A. where, in 1936, an increase of nearly 40 per cent. over the production in 1935 is recorded. Wood distillation is still responsible for about 20 per cent. of the production, the remainder being synthesised from water gas. It is reported that isobutyl alcohol, obtained as a by-product in the methanol synthesis, is available in large quantities in Russia.

Ethers and Esters

Isopropyl ether is now being produced in large quantities in the U.S.A. from synthetic isopropyl alcohol, and is finding a ready market as a low-boiling solvent. It is less volatile than ethyl ether, and is replacing it to a large extent for a number of purposes. Besides its use as a solvent it has been found to be an extremely useful blending agent and anti-knocking agent in aviation motor fuels, large quantities being used for this purpose.

Statistics show a notable increase in the production of the well-known esters, such as butyl, ethyl and amyl acetates, and a number of attempts have been made to produce these esters by a vapour phase catalytic process. Russian workers have described the use of copper-zirconia and copper-cerium oxide catalysts for this purpose and yields of esters up to 65 per cent. have been obtained. It still seems that much improved results will have to be acquired before the liquid-phase esterification is replaced. By the catalytic esterification of glycol with acetic acid, only glycol diacetate is obtained.

Synthesis of Ethyl Acetate

A promising synthesis of ethyl acetate, which has been known for some time, is by the condensation of acetaldehyde in the presence of an aluminium butylate catalyst. Recent work has shown that by the use of toluene as a solvent, and by the addition of a trace of aluminium chloride to the catalyst, 86 per cent. yields of the ester can be obtained. A further synthesis of esters which is likely to assume considerable importance in the future, is from the ethers obtained as by-products in the production of alcohols from olefines. By treating the ethers with sulphuric acid and acetic acid, it is possible in this way to obtain isopropyl and isobutyl acetates in good yield. Esters can also be produced by treating with an organic acid the acid liquor obtained by absorbing olefines in sulphuric acid. A 61 per cent. yield of isopropyl acetate can be obtained in this way. The direct combination of olefines with organic acids, which would appear to be an attractive method for synthesising esters, takes place only with considerable difficulty, and pressures up to 1,000 atmospheres appear to be necessary. Among the newer esters described may be mentioned glycerol mono-lactate and glycerol mono-oleate, the former being produced by the interaction of glycerol and ethyl lactate. An interesting unsaturated ester recently described in crotyl butyl phthalate.

Considerable activity has occurred in the direct catalytic

production of acetone from acetylene. Although this has been patented for some years, it is only within the last few months that the process has been carried out on an extensive scale. It is reported that Shawinigan Chemicals, Ltd., of Canada, and the Société Industrielle des Dérivés de l'Acetylène, in France, are now manufacturing acetone by this method, the latter company producing 100 tons of acetone per month. Other investigators have examined the suitability of iron oxide-calcium oxide catalysts for converting ethyl alcohol into acetone and copper oxide-zinc oxide catalysts for converting acetaldehyde into acetone. A further interesting method of producing acetone is by passing the dilute acetic acid, obtained as a by-product in cellulose acetate production, over a catalyst consisting of thorium and titanium acetates.

Another ketone which is rapidly assuming importance is methyl ethyl ketone. It can be readily produced from secondary butanol, obtained from cracking gas butylene. Excellent yields of the ketone can be produced by passing the alcohol over a dehydrogenating catalyst, such as copper containing a trace of uranium. Other ketones, for example, methyl isopropyl ketone and di-isopropyl ketone, in conjunction with aqueous methanol, have been proposed as softening agents for nitrocellulose. Diacetone alcohol has been found to be a useful solvent in printing pastes and in the dyestuffs industry.

Glycols and Glycol Ethers

This important class of solvents is receiving a great deal of attention and many methods for their production have been closely investigated. Whereas previously ethylene glycol was produced almost entirely by the hydrolysis of ethylene chlorhydrine, recent research has been directed to the combination of ethylene and oxygen to form ethylene oxide, which in turn can be reacted with water or alcohols to give glycols and glycol ethers respectively. The use of specially-designed plant and carefully prepared silver catalysts has made possible the production of ethylene oxide in this way. To convert the ethylene oxide into ethylene glycol mono-ethyl ether, a number of processes have been proposed. One method is by autoclaving a mixture of ethylene oxide and absolute alcohol with sulphuric acid, while a promising catalytic process consists in the continuous passage of a mixture of the olefine oxide and absolute alcohol over reduced tungsten oxide. Another synthesis of glycol ethers is by the interaction of a glycol and an olefine, and the production of ethylene glycol mono-sec. butyl ether by this process has been described. Glycol diethers can be obtained by heating the mono-ethers with a small amount of sulphuric acid.

These ethers, which have become important components of nitrocellulose lacquers, continue to find new outlets particularly in the textile industry. Ethylene glycol mono-ethyl ether has, for example, been used for pasting dyestuffs as it increases the solubility of several colours. Diethylene glycol mono-ethyl ether has a similar application, and is principally used as a substitute for glycerine in basic printing. An aqueous solution of ethylene glycol mono-ethyl ether has proved to be a satisfactory solvent for cellulose acetate of low acetyl content. The glycols themselves have found some applications as solvents, and ethylene glycol has been found to be superior, in some cases, to ethyl alcohol as a solvent for certain flavouring essences. It has also been found to be a suitable solvent for colours in silk-dyeing.

The ethanolamines, obtained by the interaction of ethylene oxide and ammonia, have rapidly come to the fore as wetting agents, and as yarn lubricants in the textile industries. An interesting new use for monoethanolamine is as a solvent for mercury fulminate, which can be recovered by dilution or acidification with acetic acid.

Miscellaneous Solvents

Work at the Mellon Institute on the basic solvents such as ethylene diamine, the piperazines and the morpholines, has been continued, and a number of promising new outlets have been found for these substances and their derivatives. An interesting new basic solvent, marketed in this country, is cyclohexylamine, which has a boiling point of 135° C., and possesses high solvent power for many classes of dyes, and promises to be of considerable interest as an emulsifying agent and as a solvent in textile dyeing and printing.

Mesityl oxide, a derivative of acetone, has been found to be an excellent solvent for certain vinyl resins and synthetic rubbers. A new method of making bottle caps from cellulose triacetate makes use of the fact that this substance is soluble only at raised temperatures in such substances as diacetone alcohol, benzyl alcohol and ethyl lactate. The process consists in casting a hot solution of cellulose triacetate on a former, and subsequently cooling and washing the cap with water or alcohol to remove superfluous solvent. Mention should also be made of the recently-developed use of triethylene glycol and mixtures of benzol and methyl ethyl ketone for dewaxing lubricating oils.

Chlorinated Solvents

Of the chlorinated solvents, methylene chloride is becoming increasingly important as a solvent for cellulose triacetate which is insoluble at ordinary temperatures in the commoner organic solvents of the hydrocarbon, ketone or ester classes. A newcomer to this class, which still finds important outlets in the dry-cleaning and degreasing trades, is trichloro-trifluoro-ethane, which is a non-toxic, non-inflammable solvent boiling at 47° C.

In view of the commercial production of cellulose mixed esters such as cellulose acetate propionate and cellulose acetate butyrate, a paper in *Ind. Eng. Chem.*, 1936, *28*, 1310, showing the solubility of these substances in a number of organic solvents is of considerable interest. A further paper in the same journal deals with the vapour pressure characteristics of the high-boiling solvents such as the phthalates and the esters of the glycol ethers. Another interesting paper referred to in *Brit. Chem. Absts. B.*, 1937, 63, reviews the methods of testing solvent mixtures for solvent power, evaporation rates and blush resistance. A great deal of work has been published on the toxicity and physiological effects of industrial solvents, and a recent publication of the Medical Research Council ("Toxicity of Industrial Solvents." Compiled by E. Browning under the direction of the Committee of Industrial Solvents, and published by H.M. Stationery Office) gives a careful bibliography of the subject.

Plasticisers

On reading the reports of workers on plasticisers, one cannot but be struck by the number of times the conclusion is reached that, generally speaking, the old-established plasticisers have proved to be the most satisfactory. This is especially the case with the alkyl phthalates, which, apart from their plasticising action, diminish inflammability very considerably. Dibutyl phthalate has been found to be a suitable plasticiser for use with ethyl cellulose in the production of quick-setting adhesives. It has also been found that benzyl butyl phthalate and trivinyl urea give increased weather resistance to nitrocellulose films. If the films contain resins in addition to nitrocellulose, divinyl phthalate has been found to be a useful plasticiser. Another new commercial plasticiser is tributyl phosphate, which not only reduces the inflammation of nitrocellulose films, but also reduces the tendency to yellow.

Three recently developed plasticisers, obtained from a somewhat unexpected source, are the sugar derivatives sucrose octa-acetate and the ethers of mannitol and sorbitol. Sucrose octa-acetate has been shown to impart flexibility and resistance to penetration of moisture.

AN aluminium producing company is being established by the Riken concern, with a capital of 10 million yen, at Chinnampo, in Korea. Raw material is available in the shape of hard clay deposits.

Chemical Trade During 1937

The Trend in Market Prices

THE year 1937 has not been noted for any spectacular developments in the chemical industry, but the period can be marked as one of steady and unmistakable domestic progress. In the chemical markets a cheerful tone persisted throughout the year and in the general movement of chemical products into consumption the expansion has been far from disappointing, and in many respects it has amply justified the optimistic feeling that prevailed in the markets during the closing months of the previous year.

At the producing end of the chemical trade operations during the period under review continued to advance along satisfactory lines and production, if not quite attaining the high level enjoyed in the home market by the larger trades, shared to a greater extent in the genrally improved conditions. The rapid development in many of the consuming industries reacted favourably on the demand for chemicals employed as raw materials. It is impossible to say to what extent the demand has been stimulated directly or indirectly by the national defence programme. There is no doubt that it has been a dominating factor, but it is also reasonable to assume that a recovery in the purely economic field has played by no means an unimportant part in the increased activity of the markets.

Prices Remain Fairly Steady

With few exceptions prices for chemical products during 1937 remained fairly steady. Quotations, if anything, showed an upward tendency and in the closing months of the year the tone throughout all sections of the market has been decidedly firm. For many products the contract price arrangements for 1938 delivery are slightly higher than the 1937 level, and for their reason a cautious policy is being adopted in some quarters. Generally speaking, however, buyers for many of the important consuming industries are inclined to take a long view and place their requirements for the next six to twelve months, and the flow of contract business in chemicals for delivery during 1938 has been of satisfactory dimensions and in the aggregate probably greater than for previous years.

As has already been indicated the trend of quotations for industrial chemicals during the period under review has inclined rather to higher levels, but there have been one or two exceptions; for instance, ACETONE at £45 to £47 per ton is about £5 per ton lower on the year as a result of keen competition. ARSENIC also has recorded a slight fall due mainly to an absence of demand. OXALIC ACID which is now being produced in the United Kingdom in bulk quantities is a little easier than a year ago, quotations for ton lots being about £48 5s. per ton. Lower prices are also ruling for CAUSTIC SODA, CHLORATE OF SODA and SODIUM SULPHIDE. Articles which now have an increased value compared with the same period twelve months ago include the following: ACETIC ACID, both the 80 per cent. pure and the 80 per cent. technical are £2 per ton dearer, the demand during the year being very good, existing prices are expected to hold for 1938. AMMONIUM CHLORIDE, the grey galvanising at £18 10s. per ton and fine white crystals at £17 10s. per ton, have both been subject to recent advances. Dog-tooth crystals are also higher than the 1936 level. ALUMINIUM SULPHATE, contract business for 1938 is being arranged at about 2s. 6d. per ton higher, prices throughout 1937 remained at about £17 per ton. POTASSIUM DICHROMATE at 5¼d. per lb. is a little dearer than a year ago, and SODIUM DICHROMATE is also ¼d. per lb. up at 4¼d. per lb. DI and TRISODIUM PHOSPHATES, the market has been subject to keen competition, but a slight recovery occurred during the year, and existing quotations are about 20s. per ton higher than during the previous year. SODA ASH, an increase of 5s. per ton was notified by the makers in the latter part of the year, the present quotation being £5 17s. 6d. per ton. TARTARIC ACID, there has been little alteration in demand compared with 1936, but values advanced during the year as a result of dearer raw materials, the present price of 1s. 1¼d. per lb. is 1¼d. per lb. higher than at the commencement of the year. CITRIC ACID, the price advanced ¼d. per lb. during the year, British makers' prices now being quoted at 1s. 0¼d. per lb.; through the year foreign material was offered at competitive rates. CREAM OF TARTAR, there has been a substantial advance during the year, the present quotation of 92s. per cwt. being 13s. per cwt. higher than at the beginning of 1937. BORAX, all grades were advanced by 30s. per ton in the early part of the year; present quotations by the British makers are expected to continue for 1938. BORIC ACID, the makers' quotations for all grades were raised by 30s. per ton in the early months of 1937; existing prices are expected to continue for 1938. BARIUM CHLORIDE at about £12 per ton is 30s. per ton dearer than in 1936. AMMONIA ANHYDROUS is slightly dearer on the year at about 1s. 1d. per lb. for small lots. PERMANGANATE OF POTASH, values for the commercial grade were raised by 1½d. per lb. during 1937; existing prices are expected to remain steady. HYPOSULPHITE OF SODA, the pea crystals are 5s. per ton dearer than a year ago at £14 10s. per ton, the commercial grade at £11 5s. per ton for 2-ton lots shows an increase of 20s. per ton on the year. In rubber chemicals a better business is reported in CARBON BLACK and LAMP BLACK, quotations during the year remained steady and prices for 1938 are under consideration. LITHOPONE has enjoyed an increased consumption and quotations are £1 per ton up since the commencement of the year. ZINC SULPHIDE at 1s. per lb. is also slightly dearer than a year ago. LEAD OXIDES and WHITE LEAD, throughout the year prices fluctuated with the value of the metal, reaching the highest point early in March with quotations for RED LEAD ruling at £49 10s. per ton and for WHITE LEAD at £59 per ton. The decline in the prices of these products has more than offset the gains recorded in the early months of the year, and existing quotations are about £4 per ton lower than those ruling a year ago.

Coal Tar Products Fluctuate

In other directions very few alterations of any importance can be recorded. Most of the POTASH and SODA products followed a very even trend and any changes in quotations that may be made for 1938 are generally expected to incline to a higher level. Prices for FORMIC ACID, HEXAMINE, LACTIC ACID and PARALDEHYDE remained unchanged during the year and present quotations for these products are expected to continue. FORMALDEHYDE enjoyed a better demand during 1937 than in the previous year. Business was very keen but the quotation at £22 to £23 per ton remained steady throughout the year.

The values for coal tar products fluctuated throughout 1937, prices reaching the highest level about the middle of the year. Quotations for a number of products are now considerably below peak level, but still remain higher than the prices prevailing at the commencement of the year. The general demand for coal tar products was better during 1937 than in the previous year, and steady conditions are expected to continue for some time ahead. Any expansion in the demand is likely to bring about dearer quotations.

OWING to heavy pressure on our columns this week we have been obliged to hold over articles by T. L. Garner on the chemical developments in the rubber industry, and by Dr. Harry Barron on plastics in 1937, together with some reviews of societies' activities during the year. It is hoped to publish these next week.

The Institution of Chemical Engineers

Dr. W. Cullen's Presidential Greeting

THE Institution of Chemical Engineers, one of the youngest of the technical qualifying bodies, shows every sign of increasing its influence and importance. The membership is steadily rising, notwithstanding the fact that there has been no relaxation in the standard of requirements so far as experience goes or in the qualifications for graduate and associate membership.

The new session, which opened with a most successful meeting at Newcastle, on October 8, will be unique in many ways as compared with previous sessions, as a good many of the papers are held jointly with other engineering bodies, namely, the Institution of Civil Engineers, the Institution of Mechanical Engineers, and the Institution of Electrical Engineers. So far as the present session has gone the interest of members has been well maintained as is evidenced by excellent attendance at the meetings, which are now held at the rooms of the Geological Society of London.

The students section, to which the council attaches very great importance, has also started the session well, and, thanks to an energetic committee and equally energetic honorary officials, the present session shows every sign of maintaining the high standard of past years.

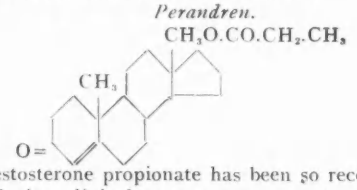
It is the devout wish of all of us that the season of goodwil, which is approaching, will have an influence for good on the affairs of our distracted world during next year. I personally express the wish that you and your readers will have a happy Christmas.

Synthetic Drugs and Pharmaceuticals

(*Continued from page* 530.)

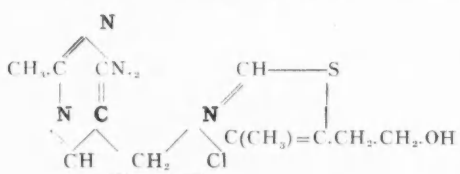
Testosterone propionate has the following formula and is issued under the name of Perandren.

Perandren.



Testosterone propionate has been so recently prepared that conclusive clinical reports are not yet available, but it has already been used in cases of prostatic hypertrophy and testicular insufficiency with much greater success than had previously been obtained by the use of testicular extracts which contain relatively a much smaller proportion of active substance.

Of the several components of the vitamin B complex the constitutions of vitamin B (Ancurin) and vitamin B_2 (lactoflavin) are well established. Vitamin B_1 has been synthesised by Williams and Cline, and independently by Todd and Bergel.



Vitamin B_1

The newly-discovered vitamin P has been shown by Szent-Gyorgyi to be closely related to hesperidin. A considerable advance has been made in our knowledge of the antirachitic vitamins by Windaus, who has established the formula of calciferol (vitamin D_2) and that of vitamin D_3 which is derived from tunny-liver oil and has shown the relationship between these two substances.

We wish to express our thanks to Dr. F. E. Driver for his kind assistance in the preparation of this article.

Oil from Coal in South Wales

Earl of Dunraven Lays Foundation Stone of New Works

THE foundation stone of the new oil-from-coal plant to be erected at Wern Tarw Colliery, Pencoed, near Bridgend, by the South Wales Coalite Co., was formally laid by the Earl of Dunraven, in the presence of a large gathering of Welsh industrial leaders, on December 16.

The Earl of Dunraven said they were commemorating the advent of an institution which would doubtless confer substantial advantages on the country generally and on South Wales in particular—a work which they hoped would be the

The ceremony of laying the foundation stone.

forerunner of others of the same kind in Wales. Twelve months ago an investigation was held at the request of the Government as to the possibility of erecting a low temperature carbonisation plant in South Wales with a view to relieving the distress that had so long existed there. This investigation resulted in the formation of the South Wales Coalite Co., under the chairmanship of Colonel W. A. Bristow.

The magnitude of the present undertaking, continued Lord Dunraven, would be gathered from the fact that the estimated expenditure upon it would come to £650,000, which included the purchase of Wern Tarw and Raglan Collieries and the cost of erecting a coalite works, together with a by-products works and a refinery. The company would make their well-known fuel, Coalite, and as soon as the works were in operation it was expected that they would carbonise 300,000 tons of coal a year. By-products would amount annually to about 5,500,000 gallons of heavy oil, 1,000,000 gallons of high-class petrol as supplied to the Air Force, and also diesel oil.

It was satisfactory to know that a large number of extra men had already been taken on, many of whom had been unemployed for years, and that during the erection of the plant a further 500 to 600 men would be required. In addition to Meiros and Raglan, the company had acquired a further area of mineral rights amounting to 1,200 acres; this would mean the opening up of a new colliery and the employment of a further 500 men.

Capt. Geoffrey Crawshay, the Assistant Commissioner for the South Wales Special Area, paid a tribute to all connected with the preliminary negotiations in connection with the present venture.

PFLANZENKAUTSCHUK-FORSCHUNGSGESELLSCHAFT m.b.H. has been formed by a group of rubber manufacturers to study the possibility of cultivating rubber-bearing plants in Germany and certain Balkan countries.

From Week to Week

AN ALUMINIUM FACTORY IS TO BE ERECTED in Amsterdam. The raw materials are, at the outset, to be imported from abroad.

GLYCERINE, LTD., report that their price for all qualities of refined glycerine for home consumption is reduced as from December 20 by £10 per ton.

MR. WILLIAM BLACKWELL, of The W. Blackwell Oil Co., Birmingham, lubricating oil manufacturers, has been elected a member of Birmingham City Council.

DR. F. G. DONNAN, D.Sc., F.R.S., has received the title of emeritus professor of chemistry on his retirement from the University chair of chemistry at University College, London.

SIR ROBERT BURROWS has been appointed a director of the L.M.S. Railway Co. He was a member of the Fuel Research Board from 1923 to 1927 and is a past vice-president of the Institute of Fuel.

THE ANNUAL DINNER AND DANCE of the Aberdeen branch of Scottish Oils and Shell-Mex, Ltd., was held at the Beach Ballroom, Aberdeen, on December 17. Mr. R. E. Reid, manager of the Aberdeen branch, presided at the dinner.

MEMBERS OF THE COMMITTEE of the newly-formed Glasgow Junior Chamber of Commerce include Mr. Colin Kennure (Alexander, Fergusson & Co., Ltd., lead paint manufacturers, Glasgow), and Mr. R. M. C. Nunneley (Richard Smith, Ltd., chemical manufacturers, Glasgow).

A REPRESENTATION HAS BEEN MADE to the Board of Trade under Section 10 (5) of the Finance Act, 1926, regarding ethyl benzoyl-benzoate. Any communication should be addressed to the Principal Assistant Secretary, Industries and Manufactures Department, Board of Trade, Great George Street, London, S.W.1, within one month from December 16.

NITROPHENYL BROWN PV, a new product of the Geigy Colour Co., Ltd., gives a full rich dark brown of good covering power when coupled with diazotised para nitraniline and also very good fastness to water, wet pressing, and perspiration. It offers a pleasing deep brown for white and coloured discharge materials, fast to water, in cotton and rayon printing.

THE NEW TEAM VALLEY TRADING ESTATE is described in a handbook, compiled by the London Press Exchange, Ltd. It is hoped that it will form a valuable addition to literature relating to the subject of the Special Areas. Copies can be obtained free of charge from North-Eastern Trading Estates, Ltd., Metrovick House, Northumberland Road, Newcastle-upon-Tyne.

METAL INFORMATION BUREAU, LTD., has changed its address to Ibex House, Minories, E.C.3. Telephone: Royal 1614-5 (unchanged).

L. STERNE AND CO., LTD., Crown Ironworks, Glasgow, have received the contract for refrigerating machinery at the new Royal Ordnance Factory at Bishopton, Renfrewshire.

AN APPEAL FOR GREATER SUPPORT from the industry for research into wool is made in a report issued by Mr. B. H. Wilsdon, director of research to the Wool Industries Research Association.

THE BOARD OF TRADE ANNOUNCE that an Order under Section 10 (5) of the Finance Act, 1926, continues the exemption from Key Industry duty till December 31, 1938, of the products specified on page 276 of THE CHEMICAL AGE, October 2, 1937.

J. W. TOWERS AND CO., LTD., report that during 1937 they introduced a new range of electrical muffle and tube furnaces for laboratory use, electric ovens of four types and a patent pipe-line connector for use with Dreadnought glass tubing. The connector, of special acid resisting unbreakable ebonite, makes the use of glass pipe-lines a practical proposition for nearly all liquids and gases.

PRACTICAL ASPECTS OF MILK formed the subject of the papers read before the Portsmouth and District Chemical Society on December 14. Mr. F. Proctor, dairy manager to Portsmouth Co-operative Society, gave an account of faults likely to develop in commercial milk supplies. Mr. R. P. Page, F.I.C., Portsmouth City Analyst, described the detection of added water in milk by the freezing point process, using the Hortvet apparatus.

PROFESSOR JAMES E. KENDALL, head of the department of chemistry at Edinburgh University, Scotland, has given $1,000 to the American Chemical Society for the 1938 American Chemical Society award in pure chemistry. This award was established in 1931 by A. C. Langmuir to encourage creative work in pure chemistry by scientists at the beginning of their careers. The age limit, hitherto 30, has been raised to 35. The secretary of the American Chemical Society will receive nominations until February 5, 1938.

THE RECENT FIRE at the Grosvenor Road Works of Fescol, Ltd., will not hold up production to any great extent. The nickel department, which is in full production, was not affected by the fire, and arrangements have been made to carry out all necessary machining of nickel deposited parts. There will be only a temporary interruption in the chromium deposition shops, but fortunately the company's new works at 39/41, North Road, London, N., are almost completed and there chromium deposition shops will be in full swing at a very early date.

The Manufacture of Paint Products and Lacquers

(*Continued from page* 533.)

[44] *Farbe u Lack.*, 1937, *35*, 413.
[45] Cole and Espenschied. *J. Phys. Chem.*, 1937, *41*, 3, 445.
[46] *Ind. & Eng. Chem. Ind. Ed.*, 1937, *29*, 6, 716.
[47] *Ind. & Eng. Chem. Ind. Ed.*, 1937, *29*, 6, 640; *Pt. Vsh. Prod. Man.*, 1937, *17*, 1, 12.
[48] *Ind. & Eng. Chem. Ind. Ed.*, 1937, *29*, 6, 656.
[49] *Z. anorg. Chem.*, 1936, *229*, 401; *Brit. Chem. Abs.*, A-111, 1937, 93.
[50] *J. Chem. Soc.*, 1936, 1,719, 1,744.
[51] *J. Chem. Soc.*, 1937, 219.
[52] F.P. 46,806.
[53] *Pt. Tech.*, 1937, *2*, 18, 193.
[54] John. *Korr. Metall.*, 1936, *12*, 12, 372.
[55] *Nature*, 1937, *140*, 3,536, 238.
[56] *N.P.V.L. Circ.*, 1937, 544, 222.
[57] *Chemistry (China)*, 1936, *3*, 691; *Chem. Abs.*, 1937, *31*, 2, 560.
[58] B.P. 459,420.
[59] F.P. 801,470.
[60] Posdnyakov and Khovanskaya. *Chem. Zentr.*, 1937, *108(i)* 2, 441.
[61] B.P. 457,076.
[62] Mertens, Hellinckx and De Hoffmann. *Brit. Chem. Abs.*, B. 1937, 60.
[63] *Pt. Manuf.*, 1937, *7*, 4, 107.
[64] B.P. 453592.
[65] D.R.P., 638,218.
[66] *Chem. Zentr.*, 1937, *108(i)* 5, 1,291.
[67] Vansheidt, Itenberg, Shtraikhman. *Chem. Abs.*, 1937, *31*, 11, 4,010.
[68] *Kunst.*, 1937, *27*, 3, 55.
[69] U.S.P., 2,085,492.
[70] F.P. 809,832.
[71] B.P. 461,495.
[72] F.P. 803,428.
[73] *Chem. Abs.*, 1937, *31*, 11, 3,870.

Oils and Fats: A Review of 1937

(*Continued from page* 528.)

interest. Glassman has studied the process of linoxyn formation and Clewell has applied the electron diffraction camera to a study of the molecular arrangements in the surface of drying linseed oil films. The extraction of wax from peat has been shown by Reilly and others to depend to a large extent on the single, double or triple solvents used and they have investigated this problem at some length.

The separation and estimation of the fatty acid components of a fat is a task usually approached with diffidence, but Harper, Hilditch and Terleski have developed a technique of fractional vacuum distillation in their study of the process of hydrogenation which is of particular interest. They have hydrogenated in stages various fish oils and shown that the process is selective. That is to say, the rate of hydrogenation of the highly unsaturated portions of the oil is much higher than that of the portions less unsaturated. In fact, in the case of whale oil, until the iodine value falls from 109 to about 50 there is hardly any increase in the fully saturated content of the oil. This has been borne out by their subsequent work with other oils. A fractionating column, designed by Longenecker, should be of assistance in similar investigations to that mentioned. It is electrically lagged and gives a very accurate control of distillation.

Summing up, therefore, the year's advance one can truly say that, from the chemist's point of view, provided that his work bears some relation to the demands of the market, fats and the industries which utilise them continue to provide an ever-expanding field for his experiment and ingenuity.

Chemical and Allied Stocks and Shares

A FURTHER contraction of business has been reported in the stock and share markets as a result of holiday influences. Nevertheless, the industrial section of the Stock Exchange maintained a firm undertone this week, and on balance numerous shares of companies connected with the chemical and allied industries have moved in favour of holders.

Distillers are 106s. at the time of writing, compared with 102s. 3d. a week ago. Imperial Chemical were virtually unchanged at 35s. 1½d. at which an apparently attractive yield is offered on the basis of last year's 8 per cent. dividend; and some market men remain hopeful that the total payment for the year may be moved up to 8½ per cent. or 9 per cent., although, it may be recalled, that in announcing the raising of the interim dividend the directors stated that an increased distribution for the year should not necessarily be anticipated. More attention was given to the new ordinary shares of Lever Brothers resulting from the Lever-Unilever merger, and on the week the price has gained 1s. 4½d. to 36s. 4½d.

Improved prices have been made by most shares of cement manufacturers on the recent announcement of the decision to raise the price of cement. Associated Portland have moved up from 86s. 3d. to 90s. 7½d. and Alpha Cement from 35s. to 36s. 9d. British Plaster Board were little changed at 28s. 3d., while Triplex Safety Glass at 51s. 9d. have recovered part of the decline shown last week. United Molasses have been active under the influence of the good impression created in the market by the statements at the recent meeting, and the price has risen from 24s. 6d. to 25s. 4½d. British Aluminium were firm and virtually unchanged at 45s. 10½d., aided by the favourable views of dividend prospects which remain current in the market, reference to which was made last week. Borax Consolidated were also well maintained at 27s. 3d., as were Pinchin Johnson at 38s. 7½d. The market is continuing to assume that there are reasonable prospects of the larger company again paying 20 per cent. for the year, despite the larger capital ranking. In September the interim payment was kept at 7½ per cent. British Oxygen were in larger demand, and at 85s. 6d. have recovered a good part of their recent decline. The market is expecting that in the early part of the New Year the latter company may make an issue of capital in connection with its Caledonian power scheme. General Refractories 10s. shares were better at 20s. 9d. at which an apparently favourable yield is offered; and some market men remain hopeful the company may raise its dividend from 16 per cent. to 18 per cent. if active conditions persist in the steel industry.

The 5s. units of Greeff-Chemicals Holdings transferred up to close on 7s. and Monsanto Chemicals 5½ per cent. preference shares remained around 22s. 6d. "middle." Ex Fison, Packard and Prentice improved to 36s. 3d. Boots Pure Drug were 3d. better at 45s. 3d.

More attention has been given to iron and steel shares, partly because of the favourable yields obtainable around current prices. Dorman Long have recovered from 32s. 6d. to 35s. at the time of writing, while Consett Iron at 11s. 4½d. show an improvement of 1s. Richard Thomas, Staveley, United Steel and Guest Keen were slightly better on balance, as were Baldwins. The current view in the market is that the latter company may raise its dividend from 10 per cent. to 15 per cent., which has to be read in relation to the moderate yield offered by the 4s. shares at their current price of 9s. 4½d. Leading oil shares fluctuated moderately, but were inclined to improve on favourable dividend estimates and on hopes that the "Shell" and Royal Dutch interim payments will be at least maintained.

Company News

Berry Wiggins and Co., Ltd., oil refiners, have declared a dividend of 5 per cent. on "A" ordinary shares, less tax (same).

National Drug and Chemical Co. of Canada announce a final dividend on 6 per cent. cumulative preference, payable March 1.

Wailes Dove Bitumastic, Ltd., makers of anti-corrosive paints, announce a final dividend of 7½ per cent., less tax, making 12½ per cent.

British Bemberg, Ltd., will not pay the coupon on its 6 per cent. debentures due on January 1, 1938, in order to conserve the funds of the company. From 1932 to 1935 the interest was paid only on a basis of 2 per cent., and the coupon due January 1 last was paid in April of this year.

British Tar Products, Ltd., in their report for the year ended September 30 show net profits (after deducting depreciation) of £64,009 (£56,904); add amount brought forward, £4,428, making £68,437; final dividend on preferred ordinary and ordinary shares of 3¾ per cent., less tax, making total of 10 per cent., less tax for the year, and bonus of 5 per cent., less tax on preferred ordinary and ordinary shares (same); write off goodwill and contracts, £9,000 (£6,000); transfer to general reserve £2,293 (nil); £3,801 forward.

British Drug Houses, Ltd., state that the usual quarterly dividend of 1¼ per cent. on preference is payable December 31.

The British Oxygen Co., Ltd., announce that a dividend of 3¼ per cent., less tax, for the half-year ending December 31, will be paid to holders of preference stock registered at close of business on December 13. Warrants will be posted on December 30.

United Indigo and Chemical Co. announce a dividend at the rate of 5 per cent. per annum, subject to tax, for six months ending December 31 in respect of preference shares.

Liebig's Extract of Meat Co. is paying a final dividend of 7 per cent., making 11 per cent., tax free, for the year to August 31 last. This compares with 10 per cent., tax free, in the previous two years, when final dividends of 6 per cent. were paid. The dividend now announced will be payable on January 26.

The Yorkshire Dyeware and Chemical Co., Ltd., announce an interim dividend of 5 per cent., less tax, in respect of the year ending March 31, 1938, payable December 31. This is at the same rate at last year's interim, but is payable on a larger capital as the new shares issued as a 25 per cent. capital bonus in June rank for payment.

Sangers, Ltd., manufacturing and wholesale chemists and druggists, announce an interim dividend of 10 per cent. actual, less tax, on the ordinary shares. Warrants will be posted on January 31. This is 1½ per cent. more than last year's interim, but it is stated that this increase is not intended as a guarantee of an increased total dividend. Last year's final was 16½ per cent.

Solidol Chemical, Ltd., in their report for the year, state that after charging management, administration and distribution expenses and directors' fees and crediting £2,676 in respect of sale and investments, there is net loss of £902, add loss on sale of shares and writing off balance of current account in Société Francaise du Lysol £29,566, and debit balance brought forward £24,917, making a debit to be carried forward of £55,385 (net loss in 1935 was £4,967.)

East India Distilleries and Sugar Factories, in their report for the year ended September 30, state that net profit was £16,378, add £8,032 brought forward, making available £24,410, of which £7,000 was absorbed by dividend paid on preference shares on July 1, 1937, leaving £17,410. The directors propose a further distribution on the preference shares, completing dividend thereon to September 30 last, and a dividend of 5 per cent. on the ordinary shares, less tax (10 per cent.), leaving £6,410 to be carried forward.

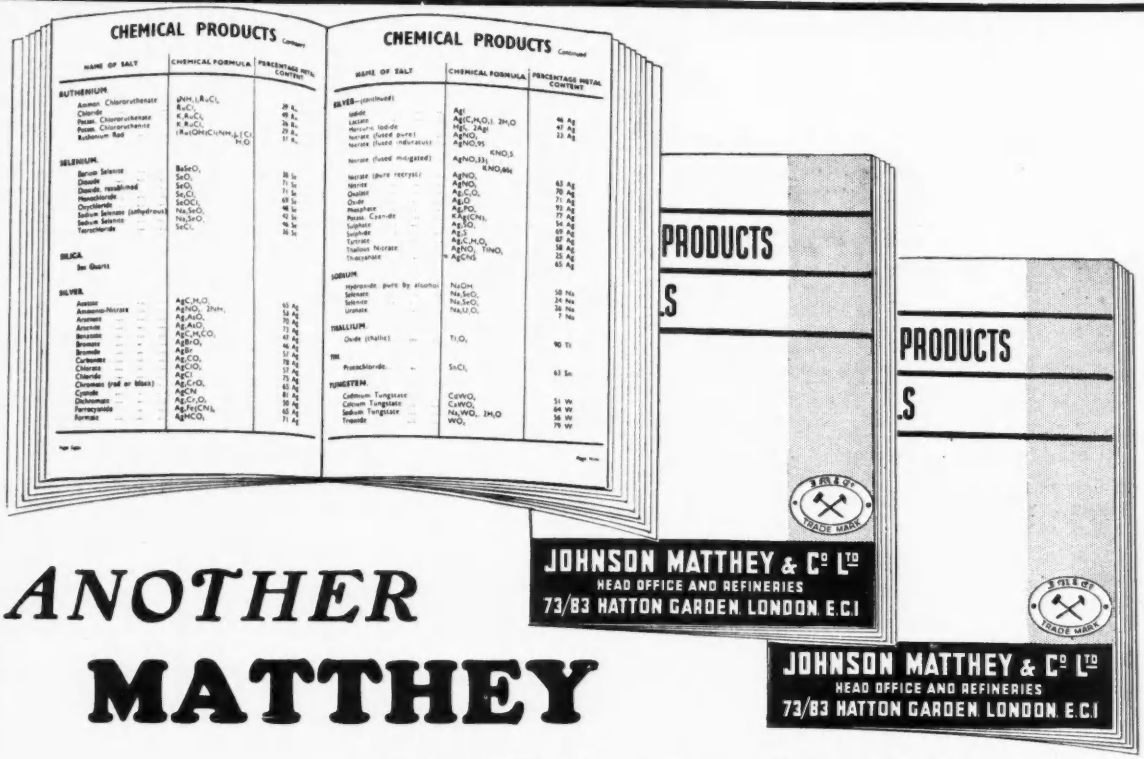
Books Received

Copper in Cast Steel and Iron. London. Copper Development Association. Pp. 136.

Outlines of Theoretical Chemistry. By Frederick H. Getman, Ph.D., and Farrington Daniels, New York: John Wiley & Sons, Inc. London: Chapman and Hall, Ltd. Pp. 662. 18s. 6d.

Metallurgical Section

Published the first Saturday in the month



ANOTHER MATTHEY *PUBLICATION*

"Chemical Products and Metals"

This new booklet will be of considerable interest to all works chemists, research chemists, research organisations, public analysts, laboratory furnishers and educational centres.

Included in the list of chemical products we supply are many unusual salts of the precious and rare metals, some of which where until quite recently, only obtainable with the greatest difficulty. The metals section of the booklet describes the many forms in which we supply precious, non-ferrous, and rare base metals. Information is also given regarding assays and analyses of ores, minerals and alloys.

Copies of publication number 31 will be sent free on request.

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Head Office and Refineries:

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Metallurgical Section

July 3, 1937

Organic Contaminants in Nickel Electrodeposition

THE presence of organic materials, e.g., wood, fabric, etc., in nickel-plating solutions tends to cause contamination of the solution, which may result in serious deterioration in the quality of the deposit. Organic impurities may be introduced into the electrolyte from various sources, i.e., from nickel salts used in the preparation and maintenance of the solutions, which contain organic materials due to contact with wooden tanks and textile filters during manufacture; secondly, from calico or felt used for anode bags, filters or salt containers, which introduce organic materials present in the cloths as dressing; and thirdly, from the wood or rubber linings of tanks.

Recent work at the Research Department, Woolwich, recently reported to the Electrodepositors' Technical Society by A. W. Hothersall and G. E. Gardam, has been directed to the study of the influence of certain typical organic materials (wood, textiles, dextrin and gelatin), and of the relative effectiveness of various methods of purification of contaminated solutions. It was found that organic impurities in the nickel solutions give rise, according to the degree of contamination, to a pitted or lustrous deposit, which may be cracked or exfoliated; the hardness and brittleness of the deposit are also increased by the presence of contaminating substances. Three methods are available for the removal of organic impurities, viz., (1) electrodeposition on scrap cathodes or "working out"; (2) adsorption on finely divided materials; and (3) oxidation.

Removal by "working out," while effective for solutions which are only slightly contaminated, becomes impracticably slow and expensive for treatment of badly contaminated solutions. A comparison of the adsorption and oxidation methods, indicated that processes involving adsorption only were less effective than oxidation methods which also involve adsorption. The best results were obtained by means of oxidation with potassium permanganate, using a modified method by which treatment can be carried out at 35° C., and boiling of the solution is obviated. Comparison of the appearance, hardness and bending properties of deposits made from the solutions before and after reconditioning indicate that the method described may be regarded as a practical and efficient means of correction for nickel solutions which are yielding defective deposits due to the presence of organic matter.

Surface Tension of Molten Enamels

THE surface tension of molten enamels, within the temperature range in which they are fired on metal shapes, has long been a matter of interest to the metal enamelling industry, because certain troublesome surface characteristics, including those known as "orange peel" and "crawling," have been supposed to be caused wholly or partly by improper surface tension. As part of a long-range investigation the surface tensions of eight commercial type enamels, representative of as many classes, are being determined at the National Bureau of Standards in the United States. The method employed is to weigh, by means of a torsion wire balance with optical lever, the amount of enamel which is supported through surface tension acting on a hollow platinum cylinder, which is suspended with its bottom edge at the normal surface level of the enamel. Due to the high apparent viscosity of enamels in this range of temperature (approximately 500 to 25,000 poises) the time required to reach equilibrium would be many hours were the system not forced to a condition near equilibrium. This precaution is therefore taken, and equilibrium is approached on both sides with satisfactory results. A "soft" ground coat and cover coat, and a "hard" ground coat, all gave results of 240 to 250 dynes per cm. for the surface tension.

Copper Production in the U.S.S.R.

SOVIET copper production has made considerable progress during the last few years. Since 1930, the production of blister copper from ore has almost doubled. In place of 35,000 tons produced in 1930, 63,000 tons were produced in 1935. In spite of this undeniable progress, however, the production of copper in the U.S.S.R. remains far behind the demands of the home market. It is stressed frequently in Soviet publications that copper is needed in large quantities, not only for industrial and construction purposes, but in ever-increasing quantities for military purposes, but to satisfy these demands, the Soviet Union was forced to import about 30,000 tons of copper in 1935. In view of the fact that new plants under construction will not produce for some time it seems probable that the U.S.S.R. will continue to import copper for the next few years. Nevertheless, Soviet copper resources are among the richest in the world, and after the completion of the two large new copper smelting plants in the Central Urals and Kazakston, production will increase considerably and rapidly. It is planned to produce about 135,000 tons of blister copper during the current year, inclusive of copper regained from scrap metal.

Nickel Boride Addition Alloys

FOLLOWING the use of boride-containing alloys as a wear and corrosion resistant facing it has been found that similar types of crystals may usefully be employed as hardening additions in steel, cast iron, copper and other basis materials. According to M. C. Smith, "Steel," 1937, *100*, 46, specially good results are obtained by the use of a nickel boride as the addition alloy. A mixture of 75 per cent. nickel with 25 per cent. boride crystals has a hardness of 56-58 on the Rockwell C scale and shows an extraordinary resistance

to acid and alkaline attack. Some alloys of extremely useful types are produced by addition of the nickel boride alloy to mild steel, cast iron and copper. The alloys are not sufficiently ductile to be rolled, forged or drawn, but may be cast without special provision for excessive shrinkage or distortion. All borides appear to favour close-grained crystallisation in iron and steel, but one particular nickel-boride mixture has outstanding properties in this respect. The hardness of mild steel containing 25 per cent. cast iron containing 5, 15 and 25 per cent. and copper containing 10 per cent. of this nickel boride mixture are tabulated and figures are given to indicate the relative acid-corrosion resistance of the three basis metals with and without the nickel boride additions. The effect of the addition on mechanical properties is described with reference to the copper-base alloy.

Aluminium Alloy Treatment

THE Vereinigte Aluminiumwerke A.G., in Germany, claims to have succeeded in improving the tensile strength and also the elongation of casting aluminium alloys by a special prolonged heat treatment. Castings of Lautal (4 per cent. copper, 2 per cent. silicon, 94 per cent. aluminium) are kept at a temperature of 500° C. for several days and then reduced to 470° to 450° before quenching. A tensile strength of 20 to 25 kilos and an elongation of 10 to 12 per cent. is thereby obtained. Further improvements in tensile strength, yield point, elongation, and reduction are gained by annealing the alloy for 20 hours at 120° C. and a second 20 hours with further change of temperature. Another aluminium copper alloy is treated by heating, quenching at 530° C., and artificial ageing at 150° C. for a period of 22 hours. Th. Goldschmidt A.G. has patented a mode of storing aluminium alloys, especially aluminium-magnesium-zinc alloys, after heat treatment in order to improve their mechanical properties. Under treatment the metal is kept alternately at and above room temperature.

Free Carbon in Tungsten Carbide

COMMERCIAL tungsten carbide usually contains some uncombined carbon, and as the amount of this element influences the character of the cutting alloys made from the carbide special attention has been given to the determination of this free carbon. The customary method is to treat the carbide with a mixture of hydrofluoric acid and nitric acid, when the true carbides dissolve leaving the uncombined carbon behind, but a new method has now been worked out in the laboratories of High Speed Steel Alloys, Ltd., Widnes. In this new method the hydrofluoric acid is replaced by phosphoric acid to avoid the need for platinum basins. In practice, 1.363 grams of the sample are weighed into a 150 ml. beaker, 5 ml. of syrupy phosphoric acid and 20 ml. of water are added and the mixture is heated to boiling point. The heat is reduced to a point just below boiling, and strong nitric acid is added a few drops at a time until further addition causes no action. The mixture, kept hot during the addition of the nitric acid, is then diluted with 80-100 ml. of water, poured on an asbestos pulp filter and washed once. About 20 ml. of a 10 per cent. solution of caustic soda (*not* potash or ammonia) is placed in the beaker and poured upon the filter in two portions. The contents of the filter are washed six times with hot distilled water, and asbestos and carbon are then transferred to a refractory boat and dried at 100-110° C., twenty minutes drying time being sufficient. It is finally covered with inert mineral matter, such as silica or alumina, and burned in oxygen in the usual manner. The weight of carbon dioxide collected, after allowing for a blank determination of carbon dioxide, is multiplied by 20 to obtain the percentage of free carbon in the sample. The blank determination for carbon dioxide is important and must not be omitted.

Oxide Films on Iron

NEW values have been obtained for the thickness of the oxide films which are responsible for the interference colours on iron, using a method for measuring the millicoulombs of electric current needed for their cathodic reduction. According to H. A. Miley, of the Metallurgical Laboratories, Cambridge University, who read a paper on the subject, before the Iron and Steel Institute in April, the apparent discrepancy between the gravimetric and optical results in the past can be explained as being due to the invisible oxide carried by the specimen at the time of the first weighing. The values now obtained agree well with chemical estimations of the thickness of the homogeneous films after removing them from the metallic basis, so that four methods have been brought into satisfactory agreement, and their differences are explained by the fact that the different methods do not measure the same things.

Having ascertained the accuracy of the new method by comparison with others, Miley has used it to measure the rate of oxygen uptake at ordinary temperatures, and his results point to rapid rate of oxidation for a short time (influenced by temperature changes, effective area, and cracking of the film resulting from abrasion or other treatment), followed by a relatively slow rate of oxidation. The observations of Vernon ("Trans. Faraday Soc.," 1935, *31*, 1674) that no bright colours appeared on iron below 200° C.—even when the amount of oxidation was sufficient to have caused colours at high temperatures—were also confirmed. Miley believes that the oxide formed below 200° C. has a cubic structure and that the oxide formed above 200° C. has hexagonal structure.

Treatment of Lead Concentrates

AT the Halkyn mine, North Wales, an electrolytic process for the production of lead and sulphur from the mill concentrates has now been in operation on a semi-commercial scale for about two years ("Bull. Inst. Mining and Metallurgy," December, 1936). The process, which depends on the electrolysis of a fused chloro-sulphide melt to produce both lead and sulphur direct from concentrates in one operation, possesses some outstanding advantages over the established pyro-metallurgical method of reduction. One feature in particular, which should commend its adoption, is that it produces sulphur direct from the ore as a saleable product; it is unnecessary to erect a costly plant for the manufacture of sulphuric acid from the sulphur gas, or alternatively, to render the gas innocuous to plant and animal life before disposing of it as a waste product. Lead of 99.95 per cent. purity, and sulphur 99.5 per cent. purity is being obtained from the concentrates. The fundamental soundness of this process having been proved, attention is now being turned to the treatment of "cell skimming."

The Electrodeposition of the Platinum Metals*

By K. SCHUMPELT, Chief Electrochemist, Baker & Co., Inc., Newark, N.J.

DURING the past ten years the electrodeposition of the platinum metals has made such rapid progress that it seems proper to analyse the causes which have aroused interest in these metals and also to survey the achievements which have been made. The textbooks on electrodeposition of metals, even those of recent date, contain only rather meagre information regarding the metals of the platinum group, and wherever formulæ for plating solutions are given they refer mostly to platinum, hinting only very vaguely that similar solutions can be made for palladium, rhodium and iridium.

When during the early years of this century white gold began to come into vogue, the jewellers very soon found themselves confronted with the serious problem that all the white gold alloys, particularly those which contained nickel as whitening metal, developed discoloration in a more or less short time. To overcome this serious drawback the manufacturers resorted to flash plating white gold articles with metals which promised to give some protection. Strange as it may seem, even chromium and tin deposits were used for this purpose on expensive solid white gold jewellery. Both metals, however, were objectionable; the former on account of the blue colour and the lack of throwing power, the latter because it stained light coloured dresses.

The only logical solution for this problem was the use of platinum as a tarnish preventing coating, and perhaps only the high cost of the metal and the lack of reliable formulæ for plating solutions account for the delay in its general application.

Platinum and Palladium Plating

The word "platinum" in itself offered a good sales argument of great appeal to the public. In order to prevent misuse or misrepresentation, a stamping law was enacted in some American States which compelled the manufacturer to apply a platinum deposit of 5 per cent. by weight of the article whenever the word "platinum" was used in connection with the gold hall-mark.

At this time the best known and most used platinum plating baths were made by boiling chloroplatinic acid, $H_2PtCl_6.6H_2O$, or ammonium platinichloride $(NH_4)_2PtCl_6$, with a mixture of sodium and ammonium phosphate solutions. This formula goes back to an old patent issued to Pilet. The change of colour of this solution from an intense orange into a faint yellow indicates the transformation of the platinichloride into a highly complex ammino-phosphate. It is this compound which produces the metal ions in sufficiently low concentration to give good deposits, even directly on base metals. This extremely low metal ion concentration is an advantage in one respect, but has two drawbacks; it causes the very low cathode efficiency which makes building up of heavy deposits a rather tedious job, and it also makes difficult the quantitative recovery of the metal from discarded solutions by the usual methods, such as "zincing out."

This platinum plating bath, like all the others of later date, is operated with insoluble platinum anodes. Therefore, the metal concentration of the bath has to be maintained by adding a soluble platinum salt, usually platinic chloride or ammonium platinum chloride. This in turn results in a rapid accumulation of chlorides. It is obvious that, due to this method of replenishing, the lifetime of such baths is very limited.

In order to satisfy the growing demand for a better platinum plating solution an extensive research was started and, in 1927, Zschiegner applied for a patent covering the transformation of platinic chloride into an ammino-nitrite of the formula $Pt(NH_3)_2(NO_2)_2$. Corresponding compounds for palladium and rhodium were also included in this application. This type of salt subsequently has become known to the trade under the name "Platinum P Salt."

It can well be said that Zschiegner's application of 1927 was the starting point for a rapid development in the plating of platinum metals. More than twenty patents have been issued since this time, and a great number of applications are still pending. The main feature of Zschiegner's plating solution was the fact that the baths did not accumulate any salts or by-products. The two radicals, NH_3 and NO_2, which were joined to the platinum in the ammino-nitrite are eliminated in gaseous form from the baths through secondary reactions. A platinum bath, 3 gals. in size, has been in practical use for several years and about 200 ozs. of metallic platinum were plated out of it before it was discarded.

Inconstancy of Catholic Efficiency

One remaining drawback to this type of solution is the inconstancy of the cathode efficiency which makes it necessary to weigh the articles from time to time whenever heavy deposits of specified weight have to be made. The platinum in the "Platinum P Salt" is bivalent, but in the plating baths it is partially changed by anodic oxidation into the tetravalent form. After the baths have been in operation for some time, there will be bivalent as well as tetravalent platinum ions present at the same time, thus causing the inconstant cathode efficiency.

The platinum baths of the "P" salt type are operated at high temperature (82—93° C.) and ammonia has to be added from time to time in order to maintain the alkaline reaction of the baths. A mixture of ammonium nitrate and sodium nitrite is used as conducting salt. White and bright flash plates can be obtained at 4—5 volts in a few seconds; heavier deposits are built up at low current densities at about 2—3 volts. Scratch-brushing of the deposit at intervals is advisable in order to facilitate the final colour buffing.

Palladium, which is available in abundant quantity and at a much lower price than platinum, has up to now not found many applications in the plating industry; and yet, in the author's opinion, palladium could be very useful—if not as a finish, at least as a protective coating. Due to its low specific gravity, palladium gives a deposit of almost twice the thickness of that of platinum, if compared weight for weight. For instance, to cover 1 sq. in. of surface with a deposit 0.001 in. in thickness, 0.345 g. of platinum would be required as against 0.195 g. of palladium. Based on the present prices for these two metals the difference is still more striking: one sq. in. of surface covered with a deposit 0.001 in. in thickness would cost $0.65 in platinum, but only $0.19 in palladium.

Rhodium Plating

During the time of the platinum plating boom, another metal of this group, rhodium, made its appearance. Due to its high price, hesitatingly offered by the producers and cautiously accepted by a few manufacturers of high-priced jewellery, it very soon conquered the whole field of jewellery and novelties, and is to-day a standard finish on almost all metal goods whenever a white, non-tarnishing finish is required.

Rhodium is one of the most inert metals of the platinum group. It is not attacked by *aqua regia*; neither do sulphur fumes affect it. Its hardness far surpasses that of platinum and palladium. Of the base metals generally used as coatings, only chromium is slightly harder. Above all, the beautiful white colour and the high lustre has opened a wide field of application for rhodium.

The first attempts in rhodium plating employed the commonly known rhodium salts, such as the chloride or the sulphate. Although depositis could be obtained from these solu

* From a paper presented at the First International Electrodeposition Conference, organised by the Electrodepositors' Technical Society, London, March, 1937.

tions, they were far from satisfactory. A rhodium bath made according to the old Pilet formula, using rhodium chloride with a mixture of sodium and ammonium phosphates, yielded deposits of a steel-blue colour and had an extremely poor throwing power.

The marked tendency of rhodium to form complex salts gave the chemist employed in this line of research many hard problems to solve. It took years of intensive effort and the co-operation of specialists in different lines of chemistry and physics before a suitable formula could be developed. A number of patents have been issued for rhodium plating solutions covering the double nitrites in acid or alkaline solutions, rhodium sulphate or chloride in combination with the corresponding aluminium salts and free acid, and rhodium ammino-cyanides.

Brilliant White Deposit

Generally, it can be said that only acid electrolytes will give brilliantly white deposits and at the same time show good throwing power. The solutions which have been most successful in the United States are of the acid type. They use rhodium sulphate dissolved in dilute sulphuric acid or phosphoric acid, or a rhodium phosphate in combination with the same acids. While the rhodium sulphate is a well-defined compound of the formula $Rh_2(SO_4)_3.12H_2O$, there seem to exist a great number of rhodium phosphates of more or less complex nature to which no definite formula can be assigned as yet. In attempting to isolate these complex phosphates in solid form they undergo changes, or decompose and make their identification difficult, if not impossible. It is only by rigorous and scientific control during manufacture that a consistent and uniform product can be obtained. This explains also why rhodium for plating purposes is now sold in the form of concentrated solutions.

U.S. Pat. 1,981,820, granted in 1934 to F. Zimmermann and H. E. Zschiegner, assignors to Baker and Co., Inc., covers very broadly the use of a complex rhodium phosphate in acid electrolytes and practically all rhodium plating solutions sold in the United States and Canada come under this patent. A typical plating solution for rhodium is made by dissolving 2 g. per litre of metal in the form of a complex phosphate in a 2 per cent. sulphuric acid solution. Insoluble platinum anodes are used, and therefore the rhodium has to be replenished by addition of a concentrated solution of the metal.

Flexibility of the Plating Bath

One great advantage of the modern rhodium plating bath is its flexibility. It can be operated successfully from room temperature up to 60° C. and the current density can vary from 10 to about 100 amps. per sq. ft. (1—11 amps. per sq. dm.). The best solutions of this type produce in 30 minutes plating time at 20 amps. per sq. ft. (2.2 amps. per sq. dm.) a bright deposit of approximately 0.00006 in. (0.00015 cm.), which does not require any buffing. The throwing power approaches that of a gold or silver plating solution. Small goods can be completely rhodium plated in a few seconds, even when suspended in bundles, and this is the reason why rhodium can compete successfully with chromium in plating small articles, despite the tremendous price difference between the two metals.

In some cases, particularly for rhodium plating white metal goods (tin alloys), a phosphate solution has been recommended. This is made with 2 g. per litre rhodium in the form of the complex rhodium phosphate and from 10—40 ml. per litre phosphoric acid. This solution has a higher resistance than the sulphuric acid baths, not quite as good a throwing power, and the deposit has a tendency to become foggy and dull round the edges.

An electrolyte of this type (in the author's opinion) has no advantage over the sulphuric acid electrolyte. Some tests have been made using two commercial rhodium preparations made by different manufacturers in sulphuric acid and phosphoric acid electrolytes. In each case 3.22 mg. of rhodium per sq dm. (0.2 mg. per sq. inch) was deposited directly on a polished sterling silver sheet at 20 amps. and 40 amps. per sq. ft. After plating, the samples were submitted simultaneously to a tarnish test (2 per cent. hydrogen sulphide gas in moist air) and the results showed clearly that strips plated in sulphuric acid electrolytes withstood the tarnishing effect better than strips plated in the phosphoric acid electrolyte.

It has been said in favour of these phosphoric acid electrolytes that they do not attack the tin alloys as readily as the sulphuric acid solutions, and therefore assure better plating results. On the other hand, tests have shown that the quality of the nickel underplate on tin alloys is the only guarantee for success. Unless the nickel deposit is perfect, faulty rhodium plates will result.

Due to the high price of rhodium the amount of deposit is in the most cases very limited. It has therefore become a common practice to use a nickel underplate in order to increase the wearing quality. The amount of rhodium plated on different kinds of merchandise varies from a mere flash on the cheapest line of jewellery up to 9.7 mg. per sq. dm. (0.6 mg. per sq. in.), equivalent to a thickness of 0.000019 cm. (7.6×10^{-6} in.) on silverware. It has been found that a deposit of this thickness gives satisfactory wear over period of years. The cost of such a deposit is approximately $0.052 per sq. dm. of surface.

A Useful Light Reflecting Metal

In addition to jewellery and silverware, rhodium has found a very important application on reflectors of any description and for any purpose. Of all the metals, rhodium approaches the most nearly to the reflectivity of freshly polished silver. Taking the reflectivity of freshly polished silver as 100, rhodium shows an average reflectivity of 78—82 over the visible range of the spectrum, and decreases only slightly in the ultra-violet region, where silver drops far below rhodium. Rhodium also has been applied to metal reflectors for high-powered movie projectors, which, after several months continuous use, have not shown any signs of deterioration. The carbon particles, which splutter from the arc on to the reflecting surface, can simply be wiped off without leaving any marks.

The question often has been asked whether rhodium deposits can be stripped. As stated before, rhodium is not attacked by any acid, not even *aqua regia*, neither is there any way to dissolve it anodically. Therefore, the question of stripping must be answered in the negative. Since, however, in almost all cases a nickel underplate is used and since the rhodium deposit is generally very thin and slightly porous, any known method of stripping nickel may give some results, taking into account the nature of the basis metal. If, for any reason, an electrolytic strip cannot be applied, there remains only one way—the mechanical removal of the rhodium by grinding and polishing.

Tinplate Decoration

A New Monograph

THERE is rather a paucity of literature on the decoration of tinplate and in view of the growing importance of the industry a monograph on the subject, entitled "The Decoration of Tinplate by Printing and Varnishing," by W. E. Hoare, B.Sc., will be welcomed.

This booklet (International Tin Research and Development Council, Technical Publication Series B, No. 4) has sections devoted to lithography, the process of tin-printing, the rotary off-set tin-printing machine, tin-printing inks, stoves and drying ovens, varnishes, the printing characteristics of tinplate and the design of printed containers.

In the section on lithography there is a brief sketch of how this process was originated by Senefelder in 1798 and of the subsequent improvements made possible by the use of metallic printing plates, rotary presses, offset methods and photolithography. The preparation and sensitisation of printing plates is described. Under stoving, the booklet discusses the troubles which are liable to occur through drying at unsuitable temperatures and speeds.

Tinplate Production by Electrodeposition

Two Notable Contributions to the Literature

PROBLEMS in connection with the production of tinplate by electrodeposition instead of by the older established hot-tinning method were discussed in a paper recently read before the Electrodepositors' Technical Society by D. J. Macnauhtan, W. H. Tait, and S. Baier, under the title "Electrodeposition and Polishing of Thin Coatings on Steel."

Recent developments in the rolling of large ingots of steel into continuous strip suitable for tinplate manufacture have created the need for a satisfactory continuous tinning process. Difficulties with the hot-tinning method have stimulated work on electrodeposition which is so often adaptable to continuous conditions. In this particular paper, the investigation of various factors affecting the nature of the tin coatings produced by continuous electrodeposition on a strip two inches wide was reported. Satisfactory coatings were obtained with both alkaline and acid baths, but the acid bath is preferred. With the acid bath it appears to be possible to electro-tin at speeds comparable with those used in hot-tinning, while keeping the length of the bath within practical limits.

Coatings vary from rough matte to smooth matte or even semi-bright, but all require polishing to make them bright. Quantitative data on polishing were obtained by means of a specially devised apparatus, allowing control of the pressure and speed of the polishing mop. By providing a transverse movement for the specimen the amount of polishing given to parallel strips could be controlled, and the drag of the specimens under the mop was also measured. With the various polishing materials investigated the loss due to polishing ranged from 7 to 20 per cent. of the weight of the coating; for smooth matte it was about 10-13 per cent. and porosity was doubled by it. Scratch-brushing caused less loss than polishing, but the porosity was much greater except in the case of brass-wire brushes which did not increase it much.

In a supplementary paper D. J. Macnaughtan and J. C. Prytherch described the "Effect of Deformation on the Protective Value of Hot-Dipped and Electrodeposited Tin Coatings on Steel." The electrodeposited coatings produced by the methods described in the previous paper were examined to see how they behaved when the strip was deformed. This is important because tinplate is usually deformed during fabrication.

To provide a basis for comparison tinplate made by hot-dipping was also put through the tests of stretching and close-bending. Commercial samples of hot-dipped tinplate with coatings of 0.00012 inch and 0.0003 inch were used and the effect on porosity was examined. The protective value of the coatings in the unstretched condition was very different from that after stretching, smooth matte coatings being greatly superior to the rough matte. The authors discuss the factors responsible for the behaviour of the tin coatings under deformation and the possible effect of the steel base.

Both of the above papers have now been issued together as Technical Publication Series A, No. 52, of the International Tin Research and Development Council, from whom copies may be obtained free of charge

Some Recent Metallurgical Patents

Annealing Alloys

Gold alloys containing beryllium contain also nickel or cobalt or both, with or without one or more of the metals copper, silver, and zinc. The alloys may be quenched from above 650° C. followed by reheating at a lower temperature. An example consists of 75 per cent. of gold, 13.5 per cent. of copper, 9.5 per cent. of nickel, and 2 per cent. of beryllium, and is heated for one hour at 700—850° C., quenched, and reheated at 320° C. for 4 hours The heat-treatment may be combined with hardening by cold working. (See Specification 455,895 of Compagnie de Produits Chimiques et Electrometallurgiques Alais, Froges, et Camargue).

Alloys containing Boron

Alloys containing boron are prepared by mixing with an alkaline earth boride, such as calcium or barium boride, the metal or metals to be alloyed with the boron, in metallic form or in the form of oxides or salts, and bringing this mixture under a layer of flux to a temperature sufficient to cause the fusion of the whole and not below 1,000° C. When using oxides or salts, these may be reduced by the boride itself, employed in quantity sufficient to effect the reduction and to provide the requisite proportion of boron in the final alloy, or by agents such as aluminium, magnesium, calcium, sodium, carbon or silicon in the presence of a suitable quantity of boride. The reaction may be effected in an electric furnace or aluminothermically. The flux may be anhydrous borax or boric anhydride. Binary alloys of boron with iron, aluminium, nickel, cobalt, manganese, chromium, molybdenum, tungsten, vanadium, titanium, tantalum, or silicon and ternary or more complex alloys of boron with any of these elements or copper, zinc, tin, antimony, or lead may be produced. (See specification 458,314 of Soc. D'Electro-Chimie, D'Electro-Metallurgie, et des Acieries Electriques D'Ugine and Andrieux, J. L.).

Corrosion Resisting Alloy

A corrosion-resistant alloy comprises 75—84.14 per cent. of copper, 7.5—11 per cent. of tin, 5—9 per cent. of lead and 3.36—5 per cent. of antimony. The tin is first alloyed with part of the copper and the lead with the antimony; the remainder of the copper is then alloyed with the lead-antimony alloy and, finally, the copper-tin alloy is added thereto. In making the lead-antimony alloy a flux consisting of equal parts of ammonium chloride, sulphur, and resin may be used, and for the final alloy phosphor copper may be used as a flux. The alloy may be used in the production of accumulator plates, valves, particularly for oil tanks, chemical plant, components which enter into contact with concentrated perfumes, condensing plant, laundry machinery, and in brewery engineering. (See Specification 456,423 of F. H. Bennett).

Extracting Iron

In a process for the separation of iron from ores containing, in addition to iron, metals which are more difficult to reduce than the iron, the ores, mixed with solid fuels, are subjected in a rotary tubular furnace at 900—1,400° C. to a reducing process such that only the iron is reduced, the sponge iron so produced being converted into lumps, the other metals remaining in the slag, by the admission of oxidising gases. The process may be applied to the treatment of bauxite to produce pure alumina. The oxide of the metals present other than iron, such as manganese chromium, tungsten and vanadium may be decomposed simultaneously with the iron by the addition of alkalies or sulphiding agents such as soda or gypsum. When these substances are added during the treatment of bauxite the final slag may be lixiviated to enable the alumina to be separated and the iron lumps and slag containing alumina may be similarly treated to obtained the alumina contained in the slag. (See Specification 457,605 of Krupp Grusonwerk Akt.-Ges.

Treating Metallic Surfaces

In order to prevent the deposition of solid or semi-solid substances, *e.g.*, carbon, from liquid organic lubricants, the inner surfaces of the cylinder walls of internal combustion engines are modified by bringing them into contact with elementary sulphur at a temperature of from 100—about 350° C. Sulphur may be deposited on the walls, for example by electrolysis of solutions of sulphides, polysulphides, thiocyanates, thiosulphates, or sulphites, the decomposition being mainly the result of electrophoresis, and the surface subjected to the elevated temperature, or an organic lubricant containing sulphur may be brought into contact with the walls at the elevated temperature. The elevated temperature required to effect the modification may be produced artificially or by the normal working of the engine, and the heating may be effected in conjunction with a supply of air. (See Specification 455,790 of J. T. Shevlin).

Heat-Treating Alloys

Alloys containing 50—75 per cent. of gold, 40—15 of platinum and 5—25 of palladium, more than 5 of palladium being present when there is more than 65 of gold, are hardened by annealing them at a temperature above 1005° C. but below their melting point and then either quenching and reheating to 500—750° C. for a time sufficient to produce the desired hardness, *e.g.*, ¼ to 1 hour, the subsequent quenching being followed, if desired, by cold working or cooling slowly to a temperature within the range 500—750° C. and then quenching. The hardening may be carried out by rolling an ingot, subjecting it to a prolonged homogenising annealing, *e.g.*, for 1—2 hours, then to short anneals, *e.g.*, for 1—5 minutes at intervals in the rolling process, each anneal being followed by quenching and then to a final heating at 500—750° C. for a time sufficient to produce the desired hardness, *e.g.*, 1—½ hour. The amount of reduction in thickness produced by the rolling is from 20 to 90 per cent. In an example, an alloy contains 70 per cent. of gold, 20 of platinum and 10 of palladium. (See Specification 456,743 of A. R. Powell, E. R. Box and Johnson, Matthey and Co.).

Extraction of Magnesium

In the extraction of magnesium from magnesium oxide or materials containing it by means of a reducing agent having a difficulty volatisable oxide such as aluminium, silicon, or calcium, the operation is carried out under reduced pressure in a melt which may consist of lime, alumina, fluorides, bauxite, clay, etc., the constituents of the melt being so selected, with the addition of fluxes is necessary, that the melting point is kept as low as possible, which enables carbon or graphite to be used for the construction of the reaction vessel or electrodes or both. The operation may be continuous. The reaction vessel is preferably enclosed in a gas-tight metal container. The reduction of a charge consisting of magnesium oxide, lime, calcium fluoride, an iron-aluminium-silicon alloy containing 41 per cent. of aluminium and 37 per cent. of silicon, and an iron-calcium-silicon alloy containing 30 per cent. of calcium and 54 per cent. of silicon, the magnesium distilling into a cooled receiver, is described. (See Specification 457,009 of Dr. A. Wacker Ges. Fur Elektrochemische Industrie Ges.

Coating with Metals

A metallic base containing iron or nickel or both these metals is impregnated with another metal by heating the base in the presence of a mixture of the impregnating metal, a metallic salt, and glycerine to a temperature below the melting point of the impregnating metal. The metallic salt may be, for example, calcium nitrate, potassium nitrate, lead acetate, calcium nitrite, calcium carbonate or sodium thiosulphite. In the impregnation of steel with copper, the steel is heated in a box to about 1,000° C. in contact with a mixture prepared by adding to copper 4—8 per cent. by weight of calcium nitrate and 3—5 per cent. by weight of glycerine. (See specification 458,854 of Leverick, F.).

Agglomerating Ores

Finely powdered material, e.g., ore dust, is before being sintered, loosened by submitting it to a stirring, whipping, or like treatment at a far higher velocity than occurs in a normal mixing operation, with simultaneous addition of moisture, e.g., by means of a spray. Additional air may also be supplied. The fuel required for the sintering may be mixed with the material prior to the loosening treatment. The loosened material may be sintered on a blast grate such as a Dwight-Lloyd apparatus. Prior to sintering the loosened material may be formed into rolls of small diameter, e.g., 1—5 mm. which may be sintered either on a blast grate or in a rotary kiln. (See Specification 454,750, F. Krupp, A.-G.).

Alloy Steels

An alloy steel particularly suitable for cutting tools, is produced by adding tantalum, niobium, vanadium, zirconium, boron, or titanium to a high carbon iron containing at least 2 per cent. of carbon whereby a suspension of the carbide of the added element is formed by the reaction thereof with the carbon in the iron. The high carbon iron may consist of white pig iron with the addition, if necessary, of solid carbon. The amount of tantalum, etc., which is added is sufficient to absorb all the carbons present in excess of 0.7 per cent., *e.g.*, up to 40 per cent., so as to enable the matrix to be hardened by heat treatment, and known steel making elements such as chromium up to 30 per cent., tungsten up to 20 per cent., and molybdenum up to 10 per cent. may be added to the matrix so produced. For the production of a steel which is capable of nitrogenisation, tantalum, or niobium is added in excess of that required to absorb the carbon in the melt, together with aluminium. The carbide may be isolated by chemical means such as treatment with hydrochloric acid for use as an abrasive or for the manufacture of tools. (See Specification 457,760 of W. M. Burden, R. Genders, and R. Harrison).

Refining Metals and Alloys

In a process for refining carbon-containing metals and alloys in an induction furnace in the presence of a reducing atmosphere obtained by expelling the initial atmosphere by means of an inert gas or vapour and subsequently removing the inert gas, etc., by the introduction of the reducing gas, the introduction and removal of the gas for expelling the atmosphere in the furnace is effected only when the bath has become practically motionless by cutting off the current and when a protecting slag layer has been formed due to the particles in the slag rising to the surface when the current is cut off. The charge is normally covered by a slag but if no slag is present a slag-forming substance is added before the current is cut off, the slag layer being removed before switching on the current again. Alternatively, when no slag is present, slag-forming substances in small amounts are added before cutting off the current, but this slag which forms a skin is not removed before the current is switched on again. Slag forming substances which are added comprise hydroxides or carbonates or mixtures thereof of the alkaline or alkaline earth metals. The process may be applied to the refining of iron or iron alloys. (See specification 458,025 of Rennerfelt, I.).

Extracting Gold

In a cyanide process in which a carbonaceous precipitant is used, the ore is ground wet with the carbon and the mixture is treated with cyanide, and thereafter the precipitated gold is removed by concentration of the carbonaceous matter from the mixture. The carbonaceous material may be charcoal or activated carbon, preferably activated carbon made from cork. The flotation agents may be added to the pulp during agitation with the cyanide. The flotation may be effected with the aid of fuel oil, blast furnace creosote, pine oil, and xanthate. Charcoal may be prepared by being crushed and heated to 850—1,000° C. in an externally heated inclined rotary kiln and thereafter quenched in water; or it may be blown with air on a forge while being stirred, and then quenched in water. (See specification 458,598 of Tennant, W. J., and Tucker, S.).

Metallurgical Section

August 7, 1937

Light Metal Production in Germany

THE German non-ferrous metal industry in 1936 experienced its most active and eventful year since the World War. Production continued at an even more accelerated rate than the two preceding years indicated, and there were far-reaching changes within the industry that resulted especially from the policy of possibly replacing imported raw materials by those of domestic origin. This policy found expression particularly in the output of light metals, notably aluminium and magnesium. The demand for these metals and their alloys, indeed, was so strenuous that it proved difficult for production to keep pace with the rapidly increasing national requirements. Efforts were also redoubled to intensify the systematic collection and recovery of old and waste metals. In addition, an intensified preference was given to imports of ores and concentrates rather than to finished metals, mainly with a view to increasing the work of German smelters. The shortage of foreign metals, particularly lead, which resulted from a stringent foreign exchange, that caused imports to decline, became even more acute and brought about even stricter official measures to limit consumption of these metals.

Despite a five-fold gain in aluminium output from 18,900 tons in 1933 to 95,200 tons in 1936, Germany was forced to supplement its needs by importing 15,000 tons in 1935 and 4,000 tons in 1936. Although much of this increased demand for aluminium has been due to the manufacture of aircraft and Germany's greater economic activity, it has been due also to the substitution of aluminium for other metals, chiefly imported and officially restricted in use. It is estimated that of Germany's total consumption of aluminium in 1936 (101,124 tons, including scrap) from 25,000 to 30,000 tons were used as a substitute metal, more particularly in place of copper and tin.

Imports of aluminium metal and scrap decreased appreciably in 1936 from the high levels which were attained in the preceding year; this decrease, especially for imported aluminium, reflects the rapid increase in German productive capacity. Present prospects indicate that the heavy demand for aluminium, both as a substitute metal and for normal purposes in competition with other metals, will continue vigorously during the current year. That aluminium will continue to be imported for supplementing the domestic output, at least until the end of September, is suggested by a recent Government decree extending the suspension of the normal import duty of 25 marks per 100 k.g. upon virgin aluminium metal. Exports of aluminium scrap are also forbidden by official decrees, except in special cases specifically approved by the competent trade control board. A further small increase in the production of bauxite during 1936 is indicated, but German producers, aware of the dangers inherent in basing such an important production branch as the aluminium industry upon foreign raw-material sources, have been conducting intensive research to develop processes to utilise domestic low-grade clay instead of bauxite for producing aluminium in an emergency.

Although it is known that Germany's production of magnesium was further expanded in 1936, no statistics are available to give a clue to the approximate amount of the output. One estimate places the yearly output at 30,000 tons; a later estimate states that the annual production probably does not exceed 20,000 tons. Nevertheless, Germany continued to be the world's largest magnesium producer, and the volume of its production was acknowledged to surpass that of the rest of the world combined. As in the cases of aluminium, the use of magnesium has been pushed intensively as a substitute for imported heavier metals. Used in the form of such alloys as " Elektron " and " Hydronalium," magnesium has been finding a steadily increasing application; due to its very light weight it is especially esteemed in the manufacture of aircraft.

At the beginning of 1936 a new magnesium plant was put into operation at Heringen. This plant, constructed by the Wintershall potash company (which controls more than 50 per cent. of the national potash output), makes use of new processes for the extraction of magnesium from carnallite, which is a low-grade potash salt. Until this plant began to operate, the entire German output of magnesium was furnished by the Bitterfeld plant of the I. G. Farbenindustrie.

Separation of Nickel from Cobalt

A STUDY of methods for separating nickel and cobalt, suitable for use under works' laboratory conditions, is reported by H. Drechsel (*Stahl und Eisen*, 1937, *57*, 587), there given as the abstract of a thesis presented at the Technical High School, Dresden. Experiments on the direct quantitative precipitation of nickel, in the presence of large amounts of cobalt, by means of diacetyldioxime, showed that quantitative separation is possible only if the original solution contains at least 4 parts of nickel to 100 parts of cobalt plus nickel. Results obtained by a method based on the difference in behaviour of nickel and cobalt towards ammonia, and utilising measurement of conductivity and determination of hydrogen ion concentration in the respective solutions, indicated that the method constituted no improvement on the hypochlorite process. In fractional precipitation with sodium hypochlorite, the most suitable pH range was found to be 2.50—3.00. Following a critical review of methods proposed for the quantitative estimation of cobalt in steel, particulars of a new volumetric method, which closely resembles the ordinary nickel titration, are also outlined by B. S. Evans (*Analyst*, 1937, *62*, 363). Here a method for the titration of nickel in the presence of

cobalt is based on the conversion of cobalt into the very stable cobalticyanide form, followed by the recovery of the nickel from its more unstable cyanide complex. An account of recommended procedure is supported by examples of results obtained on five electro-deposited nickel-cobalt alloys. Particulars are also given of a new method for the separation of cobalt from all metals interfering with the volumetric procedure.

A New Alloy of High Density

THE present-day use of large quantities of radium in beam therapy at hospitals has recently necessitated the provision of more adequate protection against the harmful effects of the gamma rays. These rays are absorbed by metals in direct proportion to the density of the metal, and for this reason the container, or so-called "bomb" is made of a material of high density. These bombs, which weigh from 50 to 100 lb., are usually made of lead; gold, although denser than lead, and therefore more suitable, is too expensive. Tungsten is the only material which has a comparable density, and is reasonably cheap, but unfortunately the high density of this metal is only attained when it has been sintered at 3,000° C. In the resulting search for a new alloy of high density, the research laboratories of the General Electric Co., Ltd., at Wembley, ultimately succeeded by mixing tungsten powder with a small proportion of a material of lower melting point so that a liquid phase was formed on heating to moderate temperature. Copper and nickel were both found to be suitable additions, and it so happened that the alloys used for the construction of radium bombs commonly contained 5 per cent. of both of these metals. The density of the alloy which was produced at Wembley, as reported by C. J. Smithells (*Nature*, 1937, *139*, 490), was between 16.3 and 16.5, or about 50 per cent. higher than that of lead. The nickel and copper were added in powder form to the tungsten powder, which was then pressed to the required shape in a steel die and heated in hydrogen at 1,450° C. for an hour. The microstructure of the resulting alloy showed particles of tungsten embedded in a matrix of copper, copper-nickel, or nickel-tungsten according to the composition employed.

Industrial Application.

Although primarily developed for radium work, tungsten alloys made on this principle are finding several industrial applications. The tensile strength of the sintered alloys is about 22 tons per square inch, but although they can be hot worked, they have very little ductility when cold. At present the largest technical application is as a contact material for heavy-current circuit breakers, the alloy being applied as a facing, brazed on to the copper contact arms. Such contacts have been used successfully to break currents of 130,000 amperes at 6,000 volts.

Metallic tungsten can be obtained by the alumino-thermic reduction of tungstic oxide, or by its reduction with hydrogen in quartz or iron tubes at a temperature of 1,200° C. According to J. A. M. van Liempt (*British Chemical Abstracts*, 1925, B, 552) the pure metal (99.3 per cent.) in powder form can be obtained in yields up to 80 per cent. of theory by the electrolysis of molten sodium tungstate at 950°, with a current density of 15 amperes per sq. cm., using a quartz crucible and tungsten electrodes. Several methods have been devised for the commercial extraction of the metal from its ores. In one process wolframite, which is essentially iron tungstate and manganous tungstate, is mixed with carbon and heated in a stream of chlorine to form tungsten oxychloride mixed with chlorides of iron and manganese; treatment with water then gives tungsten trioxide, from which metallic tungsten is produced by reduction with hydrogen or a metal such as calcium, or preferably by the electrolysis of the oxide in a fused mixture of sodium and potassium chlorides. Carbon is used as a reducing agent only where high purity of the resulting metal is not essential. Ferro-tungsten, for instance, is obtained by the direct reduction of wolframite with carbon in an electric furnace.

Thickness of Nickel Deposits

IN general, the protective value of a nickel coating on either steel or brass, even in cases where the nickel is finally covered with a thin layer of chromium, depends to a large degree upon the thickness of the deposited nickel and a certain minimum thickness is commonly specified. Rapid methods of measuring the thickness at any point are therefore desirable, but most of the methods which can be used are unfortunate in that they destroy the coating and damage the article. A. Brenner (*Journal of Research*, 1937, *18*, 565), however, now describes a non-destructive method for measuring the thickness of nickel coatings on metals such as brass and zinc. In this method, which has been worked out at the National Bureau of Standards in the United States, a simple spring balance is used to measure the force of attraction between the nickel coating and a small permanent magnet. The thickness of the nickel is indicated by the reading on a dial, which is standardised for nickel coatings of known thickness. It is believed that the method will prove useful for the factory control of the plating on such articles as brass hardware.

This new test is said to be especially applicable for nickel coatings which are deposited on non-magnetic metals and the principle on which it is based is the force of attraction between a permanent magnet and the nickel coating; this force is found to be proportional to the thickness of the coating. The apparatus is standardised by tests on nickel coatings of known thickness deposited under controlled conditions. It has been found that nickel coatings deposited under different conditions vary somewhat in magnetic properties, but that uniformity in most types of plating is obtained by heating the coated samples at 400° C. Coatings of unknown origin should therefore be annealed for a short time at 400° C. before testing. Coatings deposited from a "bright" nickel bath, containing organic addition agents, were found to be much more magnetic than those obtained from ordinary baths, and the variation was not entirely removed by annealing; certain modifications in reading are therefore recommended when testing "bright" deposits. Further tests established an error which is introduced by each per cent. of cobalt or iron present in the nickel coating. Tests have also been made to determine the effect of the presence of a nickel coating on both sides of sheet metal, as well as the effect of curvature of surface, type of underlying base metal, and superimposed chromium coatings.

Special Cast Irons of Chemical Engineering Interest

New Materials for Meeting Individual Problems

SOME special cast irons of interest in chemical engineering provided the subject of a paper which Dr. A. B. Everest, of the Mond Nickel Co., Ltd., read before the Chemical Engineering Group on July 7, during the annual meeting of the Society of Chemical Industry at Harrogate.

It is difficult to give a concise definition of cast iron, more especially since recent researches have so considerably widened the range of composition and properties available in this class of metal, said Dr. Everest. It is, however, well known that cast iron is the name give to the product of the iron foundry which, in turn, uses as its basic material pig iron produced by the direct reduction of iron ore in the blast furnace. It is generally considered primarily as an alloy of iron and carbon containing between 2.5 per cent. and 4 per cent. of the latter. In addition it contains substantial amounts of other elements, of which the most important is silicon, this determining the form of carbon in the metal. Other elements, frequently regarded as impurities, are also present; amongst these the most important are phosphorus, sulphur, and manganese. The carbon exists as iron carbide in the low silicon white irons and as graphitic carbon in the higher silicon grey cast irons. The matrix also contains inclusions of other materials, of which the most important is the phosphide eutectic present to a greater or less extent according to the composition of the original iron. Other inclusions are manganese and iron sulphides, silicates, and slag particles.

The net result of the presence of all these different constituents is that cast iron is essentially a heterogeneous material. In spite of its nature, however, it can be emphasised that from the earliest days of the chemical industry cast iron has held an important place as a material of construction. The reason for this lies perhaps primarily in the cheapness of the metal combined with the fact that it is easily cast and readily adapts itself to even the most complicated shapes, and after casting the metal is readily machined.

Limitations of Iron Castings

Whilst there are many reasons for the adoption of cast iron for chemical castings, the metal in practice is frequently found to have its limitations. In the first place, cast iron in common with all metals used in the cast form, is prone to a certain amount of unsoundness and segregation, on account of which porosity with resultant physical weakness is liable to develop, and in heavy sections particularly, such porosity and open grain may lead to lack of the usual good wear, corrosion, and heat-resisting properties of the metal. Consequently it is important to realise that in considering cast iron for the chemical industry a distinction is necessary between the properties of the cast iron itself and of the castings produced from that iron.

The development of special cast irons has been directed largely in two major directions. In the first place attention has been given to the control of the impurities and inclusions in the metal so as to minimise the interruption of the matrix by these inclusions, and consequently to produce an alloy of improved physical properties more nearly approaching those of the steels. Coupled with this improvement is the question of minimising porosity and segregation in the castings generally, thus enhancing their value and service in industry. In the second place, attention has been given to the modification of the matrix in the metal, and to-day, just as we have the heat-treatable and the corrosion-resisting steels, we now have cast irons in which, by modification of the matrix generally by means of alloy additions, special properties of heat-, wear-, and corrosion resistance previously unknown in cast iron are now available.

One of the most important influences in the development of special cast irons has been the increased use of alloy additions. It has been realised from the earliest days that by mixing metals, alloys of improved properties could be produced. The possibility of so improving cast iron was recognised many years ago, and, in fact, it is of interest to record that as early as in 1799 a patent was taken out for the manufacture of hollow vessels in cast iron alloyed with 2.5 per cent. to 25 per cent. of nickel, and claims were made for the rust-resisting quality of the final casting.

Dr. A. B. Everest.

[By courtesy of the Foundry Trade Journal

Ferro-silicon alloys produced from certain types of ore possessed a high degree of corrosion resistance, and from the realisation of this fact the high silicon irons, well known to chemical engineers, were developed in the first half of the last century. These high silicon irons containing 13 per cent. to 16 per cent. of silicon have, on account of their resistance to attack by many acids, proved of great value to the chemical industry, and in spite of their brittleness and hardness they are still used in substantial quantities.

Alloys with Many Metals

With regard to the other alloy cast irons, however, the results of the investigations carried out at the end of last century and in the early years of the present century were indefinite, and a reference to the literature shows that the conclusions obtained by different workers were in many cases contradictory. The reason for this is not difficult to find. It lies essentially in the lack of general understanding as to the properties, structure, and nature of cast iron itself, which is only within the most recent years being dispelled by research.

As a result of investigations made in recent years, cast iron is now alloyed with a wide variety of metals. These include such elements as silicon and manganese (in proportions greater than those normally found in cast iron), nickel, chromium, molybdenum, copper, vanadium, titanium, tungsten, and aluminium. Investigations have established that these elements have different effects in cast iron and many of them are subject to strict limitations. Thus vanadium and titanium are used only in small proportions and serve to refine

and deoxidise the metal; tungsten so far has been little used in cast iron and its influence is as yet not fully understood.

Copper is of great interest to-day and is being used in small proportions in castings of different types. Copper, however, suffers from the limitation that its solubility in cast iron is strictly limited, and according to the nature of the iron is given as anything between 0.5 per cent. and 3 per cent. Chromium and manganese can be added over a wide range of proportions to cast iron, but above small quantities the affinity between these elements and the carbon in the iron is so great that massive carbides are formed which render the final castings hard and difficult to machine. Alloys containing high proportions of chromium have been used recently for special applications where machining is not necessary, and these alloys are characterised by a high degree of heat resistance. They are, however, difficult to produce. Molybdenum is generally used in small proportions; it tends to form carbides, which limits its usefulness in castings. Aluminium has been investigated thoroughly and an interesting series of alloys produced. In this case again, however, production difficulties, notably the occurrence of unsoundness due to alumina, have hampered the development of aluminium cast irons on a commercial scale.

Useful Addition of Nickel

Nickel, on the other hand, has proved the most useful of the alloy additions to cast iron. It can be alloyed with cast iron in all proportions, giving a series of metals with a wide range of properties which offer combinations of qualities of interest in many types of special applications in the chemical and allied industries; the usefulness of nickel is also further enhanced by the fact that it is stable in the casting, not being lost by oxidation on remelting.

Small additions of nickel up to 2 per cent. have proved useful in controlling the grain size and physical properties of good-quality cast iron, so that, as detailed below, these alloy cast irons have proved of value where castings of improved quality are required. Additions above 2 per cent., as in the case of the steels, harden the matrix. At about 5 per cent. of nickel, the alloys are air- or self-hardening, owing to the influence of nickel in lowering the critical points at which constitutional change takes place in the metal. At this percentage of alloy addition the matrix of the iron is in the hard martensitic form. These irons are machined only with difficulty, but are of special interest for their abrasion resistance, though not perhaps of great value from the corrosion-resisting point of view.

Further additions of nickel result in a series of irons of gradually decreasing hardness, until round about 16 to 20 per cent. the castings are soft again and may be easily machined. The decrease in hardness is due to the gradual replacement of the martensitic matrix by austenite, this change being complete at about 20 per cent. of nickel. The austenitic cast irons are corrosion- and heat-resistant and show at the same time good resistance to abrasion and wear. It is this series of alloy cast irons which has, perhaps, proved of greatest interest to chemical engineers.

The interest in the low-alloy cast irons (*i.e.*, cast irons containing up to 2 per cent. of special elements) does not lie primarily in the influence of alloy additions on the corrosion-resistance of the metal itself. Such alloy additions, however, have a profound indirect effect on the quality of the castings, and it is this indirect effect which is of the greatest importance to the chemical industry, especially since the use of such alloy additions nearly always demands improved foundry technique and control over the metal, resulting in greater uniformity, density, and quality in the castings.

This point is perhaps brought home best by considering the case of cast-iron pots for concentrating caustic liquors. In the case of castings of this type, manufacturers from time to time have experienced considerable trouble due to localised attack. In fact it is quite a common experience to find that pots, which have been in service for only one or two weeks, have failed due to a hole eaten straight through the bottom of the pot. In a case of this type, the metal in the pot itself, except for the localised attack, is hardly affected at all, but the localised attack has resulted in the speedy and premature failure of the casting as a whole. It has now been established, however, that the greater uniformity with freedom from porosity and segregation offered by a low alloy cast iron is effective in eliminating such local attack and thus ensuring a long useful life for the casting.

Whilst the influence of small additions of nickel in promoting soundness and uniformity in the castings is of such vital importance and should appeal to all manufacturers of chemical plant, it must not be overlooked that alloy additions do actually have a small but definite influence in improving the resistance of cast iron to many types of chemical attack. For example, nickel improves the resistance of iron castings to caustic liquors, and it is reported that on the Continent even 3 per cent. or 5 per cent. of nickel is frequently used in caustic pots and other castings for the chemical trade.

In the low-alloy cast iron good control over the composition of the base iron is essential in order to obtain the best results from the alloy addition. The quantity of the carbon must be kept low. Silicon must also be kept under control in order that nickel may exert to the full its refining effect on the form of the carbon. Phosphorus must also be kept low, since this element forms a complex eutectic which is of a hard and brittle nature and has a deleterious effect on the mechanical properties of the castings. These points must be borne in mind, since the best results from an alloy cast iron are never to be obtained if the alloy addition is made to an unsuitable grade of base iron.

High-strength Cast Irons

By the use of alloy additions, and especially by the use of special methods of preparing the base iron, it is now possible for engineers to expect a figure at least two or three times as great, and in fact it is to-day quite usual to obtain a strength of 22 to 25 tons per sq. in. in large castings. This improvement of strength is of importance in connection with many parts of chemical plant where increased stress and pressure are required, as in pump bodies, valve bodies, and reaction chambers. Or alternatively, reduction in weight may be of importance in certain types of castings, and this is now made possible by the modern high-strength alloy cast irons. A reduction in section thickness is attractive in certain castings, not only in reducing weight, but also in the increased efficiency which is available in the transfer of heat through the walls of vessels, or again in the reduction of energy required to actuate moving parts of massive section.

Wearing quality is of importance in many applications. Abrasion and erosion often account for serious deterioration of parts in service, and when coupled with corrosion they are responsible for the extremely short life experinced in certain types of equipment. The low alloy cast irons containing small proportions of nickel and chromium, giving a fine grain and superior hardness, are useful under these conditions. They are, in fact, extensively used for stirrers, impellers, and in other applications where resistance to abrasion is required. It should be mentioned, however, that under particularly severe conditions some of the harder irons described below are frequently preferable.

Ease of Machining

One of the outstanding features of the low-alloy grey cast irons is the ease with which they may be machined and the fine finish which they will take on. On this account they are especially suited for large castings in the chemical and process industries where such a finish is required. For example, in the paper industry the low alloy cast irons are being used for drying cylinders and similar applications where a high degree of finish and general all-round good quality are required with perhaps a measure of corrosion-resistance. They are also of use for rolls and drums in many types of

crushing and food-preparing plant, as, for example, in milk dryers.

Low alloy irons containing up to 1 per cent. of chromium are of special interest for heat-resisting applications, where a grey iron is desired with freedom from growth and scaling in service. Chromium itself, however, tends to render the castings brittle in service, and it is for this reason that the chromium is frequently associated with an addition of up to 1 per cent. of nickel in order to ensure toughness in service.

Cast irons containing an intermediate proportion of alloy addition, as for example in the range 2 per cent. to 6 per cent., generally fall into the class of irons specially developed for improved wear resistance. Additions of chromium or manganese in this range result in hard and unmachinable castings, whilst nickel additions of the same order give a gradual increase in hardness with increasing difficulty in machining. In the case of chromium and manganese the hardness is due to the presence of massive carbides. In the case of nickel, however, it is due to hardening of the matrix, this gradually being rendered sorbitic and martensitic, these being the structures normally associated with hard tool steel. None of the alloy irons of this type has any very special virtue in the direction of corrosion resistance. All the irons, however, are of interest on account of their superior abrasion resistance.

Very Hard Cast Irons

Up to about 3½ per cent. of nickel the irons, whilst of increased hardness, are still machinable, and this type of alloy iron is of interest where a high degree of abrasion resistance is required coupled with machinability. Above 3½ per cent. of nickel the matrix becomes so hard and tough that machining is not possible or only carried out with difficulty. These irons are used for gears, pump parts, and other applications where a combination of toughness and resistance to wear is required.

If an even harder material is desired, then consideration can be given to the very hard white cast iron known as "Ni-Hard," in which the effect of chromium in the production of massive carbides is combined with the effect of nickel in giving maximum hardness of the matrix of the metal. White irons containing 4½ per cent. of nickel and 1½ per cent. of chromium ("Ni-Hard") have the highest hardness known among any of the cast commercial metals. Their abrasion resistance is correspondingly high, especially since the hardness is combined with toughness. Such irons are used for pump impellers and other castings subjected to extreme abrasion, whilst they are of special interest in crushing and grinding applications of all types where long life in service is essential.

Further additions of nickel with or without other elements lead to the development of the austenitic type of matrix. Between 6 per cent. and 16 per cent. nickel a mixed structure is obtained in which martensite gradually gives place to austenite. Austenite is itself tough and corrosion-resistant, and some of the irons of intermediate composition have been found of special interest where a combination of abrasion and corrosion has to be encountered. Thus cast irons containing 7 to 8 per cent. of nickel with 2 to 3 per cent. chromium have been used recently for pump impellers and for other parts subject to light abrasion. Recent tests have shown that such irons possess many times the life of the harder white irons or of the special steels for high velocity pumping.

The first definite reference to the austenitic cast irons is, perhaps, that made by Dawson in 1923, who put on the market his non-magnetic alloy cast iron now known and used extensively under the name of "Nomag." In developing this iron Dawson found that cast iron alloyed with substantial proportions of nickel and manganese was soft and machinable and had the unusual characteristics of being non-magnetic and possessing a very high electrical resistance. This combination of properties was of special importance to the electrical industry, where non-magnetic alloys of high resistance were comparatively rare. The composition ultimately selected for "Nomag" was one containing nickel 10 to 12 per cent., and manganese 5 to 6 per cent.

Recent work on alloy cast irons has shown that other elements are also of importance in producing the austenitic structure. In addition to nickel and manganese as mentioned above, copper, chromium, and aluminium are also helpful but, as already explained, of these manganese, copper, and chromium all suffer from serious limitations and cannot be used by themselves. It is now appreciated that about 20 per cent. of nickel alone will give a completely austenitic cast iron. In combination with the other elements mentioned, however, nickel may be reduced substantially, being replaced in part by proportions of copper, which it carries into solution, or by manganese or chromium, in which case the carbide-forming tendencies of these elements are counteracted within limits by the presence of nickel. Aluminium has been found to give austenic structures, but the irons in addition to being difficult to cast are unstable, since the carbon present tends to form aluminium carbide.

Two Commercial Alloys

In addition to "Nomag" two other types of alloy known respectively as "Ni-Resist" and "Nicrosilal" are now well established in industry. The first of these is produced by the addition of nickel and copper, generally as the alloy "Monel," to give a composition of approximately 14 per cent. nickel and 6 per cent. copper to which is also added 2 per cent. chromium; whilst in the case of "Nicrosilal" a copper-free composition is used with about 18 per cent. nickel and in which an abnormally high silicon content has been adopted, this element generally being in the range from 4 per cent. to 6 per cent.

"Nomag" is the cheapest of these austenitic irons, but whilst eminently satisfactory for the applications in the electrical industry for which it was developed, it is not of such great interest to the chemical industry owing to its inferior corrosion resistance. "Ni-Resist," on the other hand, shows better corrosion-resisting properties and has been widely developed on this account. Its other properties, such as wear resistance and heat resistance, are also good. "Nicrosilal" combines the good corrosion resistance of "Ni-Resist" with a superior heat and oxidation resistance, and it is thus of special interest and value for applications at high temperatures.

Points from the Discussion

Professor B. O. BANNISTER (Liverpool) said they were all indebted to Dr. Everest for putting before them the very latest developments in those special cast irons. It would seem to some that in the question of alloy cast irons they were something like 20 or 30 years behind a similar situation in the case of alloy steels, and there must be some reason for it. He was glad that Dr. Everest mentioned the work of Professor Turner, who had been honoured just recently for his early work on the manufacture of cast iron castings. Turner showed the effects of those elements which were always present in cast iron. More recently that had been followed up by the work of the British Cast Iron Research Association, which had prepared the ground for the later work relating to the addition of those alloys. He would like to make it quite clear that the difference between steels—ordinary carbon steels—and ordinary cast irons in the first place was that in steel they had 99 per cent. of iron and 1 per cent. of other elements, in cast iron they had 90 per cent. only of iron and 10 per cent. of variants, so that there was very much more possibility of going wrong with those other

variants, especially as they could exist in the iron itself in very different conditions. A very little difference in those conditions would make a huge difference to the properties of the casting.

The next thing was that for many years they had looked on iron castings as the cheapest material they could get for some definite purpose, and from that point of view they had expected too much from it. They had always expected a cheap material. In the early days additions especially of nickel and chromium did so much for steel that it was asked must they not do the same for cast iron? And so they rushed forward and added nickel and chromium for cast iron, but they did not take precautions with the cast iron. To a cheap casting they added 2 to 5 per cent. of an expensive alloy like nickel, but now the importance has been realised of putting the cast iron right first. The foundries, which were producing castings of under seven tons per sq. in., were now producing castings of 14 tons per sq. in., and if all castings were 14 tons per sq. in., he thought they would be fairly well satisfied for ordinary purposes.

Ageing of Castings

Mr. W. A. S. CALDER (Birmingham) referred to the mention by Dr. Everest of "caustic pots," which were large castings that had a very heavy duty to perform. It was extraordinary, he said, how the skill of the craftsmen in the making of these castings had anticipated the researches of science. There were one or two cast iron founders who could cast those caustic pots, which had a life of 12,000 tons of caustic, or a run of 12 or 18 months, compared with an ordinary producer's casting which would not survive for more than a few hundred tons. There was a very interesting point in connection with those large castings of ordinary cast iron, *i.e.*, the extraordinary result of the ageing of the casting. If such a casting had been well aged—not less than six months, but preferably 12—the life of the pot was doubled. It would be interesting to know whether in the case of the alloy iron casting this ageing process was necessary.

Mr. J. ARTHUR REAVELL (London) said what he felt about the subject had been brought out by Professor Bannister, namely, the point that they started with such a poor basis in the case of iron. If they could only get their cast iron down to something like 99.5 per cent. purity and then add the dope—whether nickel or any other of the alloys—they might get somewhere. It was interesting to know the work that was going on in the production of pure iron. When the pure iron was produced, then with the alloys they would have produced castings which would have the benefits which they all appreciated in cast iron without the disadvantages that there were in steel.

Mr. FOSTER SPROXTON (Colchester) said one of the problems in the plastic industry was the cooling of the cast iron rolls. One must have a very hard iron and a very thick shell, because the stresses were very great and the cooling of the rolls was quite a difficulty. He wondered if there was any appreciable difference in conductivity in the irons described by Dr. Everest.

Mr. W. WOODHOUSE said reference had been made to the fact that they got very poor iron for a basis. He wondered if they had tried any of the refined irons. These refined irons were a definitely good basis. He asked Dr. Everest if he recommended denseness in the thicker sections so as to bring down the cooling range equivalent to the quicker range in the thinner sections.

The CHAIRMAN said he recognised the difficulties that chemists had in discussing a metallurgical problem. He started his career as a chemist in an iron and steel works. That was a long time ago and all they thought of then was getting a good grey iron for the foundry. Then Turner came along and showed them how to get a whiter iron with the addition of silicon, and that gave the Scottish iron trade a little boom because they were making a high grade, high carbon pig, namely, silicon pig. It was a long step from that to what they had been hearing about that morning.

In regard to foundry difficulties, it was not a question altogether of getting a pure material. A man could spoil pure material. Foundry practice was the most important thing and he took his hat off to the foundry man, who did some wonderful work. But he was conservative and he thought it would take him a little time to get into the use of those special irons. The special irons were also very expensive; he had figured it out that 15 per cent. nickel would mean something like £25 per ton. This was apart from foundry practice and special processes, so that he thought that—at first—on account of their cost there would be a limited application of those high grade irons. The lower price article even if it had to be replaced often might be cheaper than having a high grade material lasting longer. In cases like the pots shipped to the Colonies, where their own foundries were sufficient to do the repairs, and the scrap could be used, and where they might not be able to handle the special cast irons, he thought they would still continue to use fairly good cast irons rather than the austenitic iron. It would be interesting to hear more from Dr. Everest as to how the special cast irons were made.

Spun Iron Pipes

Mr. J. W. NAPIER (Alloa) said the industry he was connected with had been going in for steel pipes because of their greater length—about 45 ft., as compared with 9 ft.—and although the steel manufacturers had risen to the occasion in giving a very satisfactory coating, in gas engineering they would like to go back to cast iron and the tendency very definitely in the last year or two had been in that direction. He asked Dr. Everest whether spun cast iron pipes to which he had not referred offer any advantage or if there were any inherent disadvantage with regard to the use of such pipes for gas distribution having regard to the differences in the composition of soil throughout not only a few years time but many decades of time. He asked the question because the cost of re-laying pipes was a very serious one.

Mr. WOODHOUSE asked if he might be privileged to answer the question relating to spun iron pipes. He represented the Stanton Iron Co., and he believed they were the biggest makers of cast iron pipes in Europe. At any rate they were the pioneers of the Stanton cast iron pipe by a process which has now been operating for about 18 years. They made the pipes in diameters from 2 to 22 inches, and up to 18 ft. in length, and he could assure the speaker who had asked the question that the spun iron pipe compared favourably in many ways with the steel pipes. Corrosion was less than with steel pipes. The spun cast iron pipe was definitely of advantage especially if it was used with the Wilson joint which was flexible and was a great service.

Mr. NAPIER asked if Mr. Woodhouse would say whether the advantage was chemical or only mechanical.

Mr. WOODHOUSE replied that the advantage was not only mechanical—it was very strong. They got a tensile strength on 2 to 6 inch pipes up to 21 tons; on the 9 to 12 inch pipes, 18 tons; and on the 22 inch pipes, 16 to 17 tons. Mechanically it differed considerably from the old cast iron and had a high mechanical strength. From the chemical point of view there were no large areas for chemical attack to start with, and therefore the chemical attack was less than with cast iron and its strength compared very well with steel. Finally, the corrosive effect was less than with steel.

Dr. EVEREST, in reply, thanked Professor Bannister for his remarks, and said they undoubtedly owed a great debt to Professor Turner for putting cast iron on the map. It was he who started to get to the bottom of those variables which were obscuring the behaviour of cast iron. Professor Bannister also mentioned the question of costs, and question of cast iron being a rough job. Apart from the question of alloys they had now got down to making the metal under conditions of close control. With regard to caustic pots and the ageing of the casting the alloy cast irons were generally better and he thought he could say that they would not need the ageing that the older castings did.

Metallurgical Section

September 4, 1937

"Featherweight" Metals

THERE is a great future awaiting "featherweight" metals. This is especially evident from the developments which have taken place in Germany, more especially in the course of the last twelve months. The Leipzig Fair, which was held early this year, gave a good impression of the way in which the German metal-using industries are changing over to light metals wherever possible. Recent progress has been greatly fostered by the fact that aluminium provides a substitute metal for lead, copper and tin, all imported in large quantities even to meet normal demands. So great has been the need for conserving heavy metal supplies that even in the chemical industry, bronze used in the construction of filter plates has often been replaced by glass, with little or no advantage other than the saving of the metal.

According to the Hamburgisches Welt-Wirtschafts-Archiv, which publishes a special bulletin periodically, it was not until the beginning of 1934 that the use of aluminium in Germany reached a point corresponding with that of copper. It was the prohibitions issued at that time which turned the scales of consumption in favour of featherweight metals. The fact that featherweight metal had been used elsewhere for about thirty years in conjunction with steel, for the construction of railway vehicles, although it was only recently that efforts to start such a development had been noticeable in Germany, shows how very far Germany was behind other countries in the use of aluminium. Until 1934 about 66 per cent. of Germany's electrical network consisted of copper cables, whereas aluminium cables had been used frequently in the electrical industry in other countries. The use of aluminium-plated sheet iron also, did not gain any popularity in Germany for the armouring of conduits and pipe wires until the prohibitions were decreed, although in this direction the consumption of lead in 1933 was about 3,000 tons.

Aluminium Consumption in Germany

In 1933 the consumption of aluminium in Germany amounted to 23,800 tons; in 1932 it was only 19,100 tons, whilst at the peak of the pre-crisis boom it was 39,000 tons. Already in 1934, however, consumption had risen to 53,000 tons, or exceeded by about 30 per cent. the highest pre-crisis production. This development continued in a still greater measure in 1935, when about 93,000 tons of aluminium were consumed. During the same period in which the consumption of aluminium increased by 40,500 tons, or nearly 80 per cent., that of tin remained unchanged, the consumption of lead rose only 1,000 tons or a little more than 0.5 per cent., that of zinc 17,000 tons, or barely 10 per cent., whilst the consumption of copper fell to 272,000 tons, a decline of 15,000 tons compared with the previous year. In comparison with 1933, however, the consumption of aluminium increased 230 per cent., whilst that of zinc, copper and lead rose only 34 per cent., 20 per cent. and 13 per cent. respectively, and tin remained stationary at 17,000 tons. This development shows the direction of the change-over.

If the consumption of aluminium in Germany is compared with that of other countries, the progress made in Germany in the use of aluminium, due to the industrial boom and the change-over rendered necessary by scarcity of foreign exchange, becomes still more evident. According to one of the recent bulletins of the Hamburgisches Welt-Wirtschafts-Archiv, compared with 1933 the non-German requirements in aluminium rose only 57 per cent., so that Germany's consumption of aluminium increased about four times as strongly as in other countries, the rate of increase in the consumption of copper in Germany was only half that of non-German consumption, which increased 44 per cent. In 1933 Germany's share in the world's aluminium production had reached 12½ per cent.; in 1935 it was 25 per cent., or exactly doubled. In 1935, moreover, one-quarter of all the aluminium in the world was produced in Germany and the limit of increase in production had not been reached.

Alloys for All Needs

Pure aluminium, owing to its poor tensile strength, is used as a constructional material only in special cases; the chief uses are electro-technical and the constructing of equipment for the chemical and food industries. Aluminium foil is used as packing material, and for heat insulation purposes. For all other purposes special aluminium alloys have been evolved. During the last few years developments in this direction have been systematically pushed forward, so that "featherweight" metals of any desired quality are now available as substitute materials which compete in tensile strength with iron and steel. Copper, magnesium, silicon, manganese, nickel, antimony and zinc are used as alloy components, a further ingredient of the alloys being the iron which is present in the crude aluminium. So far as Germany is concerned, alloys are available to meet all needs. For constructions subjected to heavy strain, particularly where weight-reducing is important, as in the construction of vehicles, an alloy known as Bondur can be employed. For parts which are not subjected to such a heavy strain, but where medium tensile strength suffices and no special chemical stability is necessary, Pantal provides a substitute for brass. Lautal has a somewhat higher tensile strength, but, like Bondur, it cannot be welded because it loses its tensile strength when raised to the necessary welding temperature. Articles of everyday use are made of Mangal, which has a tensile strength about 20 per cent. greater than that of pure aluminium.

Foundry Practice for Cupro-Nickel

A SYSTEMATIC study has been made of the casting properties of 70/30 copper-nickel and a special foundry technique has been evolved by which sound castings may be regularly produced under foundry conditions. Recommended procedure, according to a paper by T. E. Kihlgren (American Foundrymen's Association, June, 1937), is to melt under slightly oxidising conditions, to oxidise the melt (with $1\frac{1}{4}$ oz. of nickel oxide or $3\frac{1}{2}$ oz. of cuprous oxide per 100 lb. of metal), and subsequently to deoxidise, 3-5 minutes before pouring, with manganese and silicon in sufficient quantity to give residual content of manganese and silicon in sufficient quantity to give residual content of 1 and $\frac{1}{2}$ per cent. respectively. If treated with silicon only, the alloy is said to be sluggish, due to the formation of a tough film or envelope around the stream of molten metal. This tendency is neutralised by the co-presence of the manganese, and a very satisfactory state of fluidity is obtained. The addition of 0.025 to 0.05 per cent. of magnesium is a useful precaution to neutralise any sulphur "pickup" which may have occurred in melting. Pouring should be carried out fairly rapidly, at a temperature of 2,500°—2,650° F.

Experimental melts made to determine the influence of small amounts of other elements on the casting properties and soundness of cupro-nickels have shown that iron up to 1.5 per cent. does not affect castability; it improves mechanical properties, but if higher than 1.5 per cent. it lowers the corrosion-resistance. Lead, however, is extremely deleterious; it produces hot shortness, excessively coarse structure, and marked unsoundness. Titanium is an unsatisfactory deoxidant and appears to have no beneficial effect on mechanical properties. Aluminium should be kept low, to prevent the formation of films on the melt. Zinc, in amounts up to 5 per cent., is inadequate to deoxidise the 30 per cent. nickel alloy, and sea-water corrosion tests of wrought alloys indicate 5 per cent. zinc to be deleterious; a maximum of 1 per cent. of zinc appears to be a reasonable limit. In silicon-free cupro-nickels, however, additions of 5 per cent. of zinc, in association with tin and lead, produced a casting of satisfactory properties. Carbon appears to exert a mildly strengthening effect, associated with lessened ductility; low-carbon melts give sounder and denser castings. Tin is believed to raise the mechanical strength of this type of alloy and to improve casting properties, but the effect of tin on corrosion-resisting qualities varies with the reagent; a maximum of 1 per cent. is suggested as being suitable.

Magnesium Production in Japan

FROM 1925 to 1930, the Tokyo laboratory of the Rikagaku Kenkyujo (Physical and Chemical Research Institute) investigated the manufacture of metallic magnesium from sea water bittern. The Rikagaku Kogyo K. K. (Physical & Chemical Development Co., Ltd.), which is an organisation for the industrial application of processes approved by the institute, first began to produce a small quantity of metal at its experimental plant at Kasiwazaki, in March, 1931, and the actual output for the year amounted to just over three tons. The Riken Magnesium K. K. (Riken Magnesium Co., Ltd.) dismantled the equipment of its own experimental plant in 1932, and then erected a new plant to produce magnesium from sea water bittern at Naoetsu. Here the initial annual production capacity of 70 tons was increased to 150 tons in 1933, and in October, 1933, this concern and other interests merged with the newly organised Nichiman Magnesium K. K. (Japan-Manchukuo Magnesium Co., Ltd.),who have constructed a new plant at Ube with a yearly capacity of 250 tons of magnesium from sea water bittern and 100 tons of metal from magnesite. The capacity of this plant was increased to 700 tons in 1936, and may be 1,000 tons by the end of the present year. The merit in combining two processes in one plant, as in the case of the plant at Ube, is that chlorine gas recovered as a by-product from the process using sea water bittern is used to convert calcined magnesite into magnesium chloride in the second process. In the first process, the production of one ton of metallic magnesium requires 17 to 20 tons of solid bittern and about 50,000 kilowatts of power.

The Nippon Magnesium Kinzoku K.K. (Japan Magnesium Metal Co., Ltd.) established a magnesium plant at Konan, Korea, in 1934, using an Austrian direct thermal reduction process, with magnesite as the raw material. This plant is still in the experimental stage, but is expected to have a yearly capacity of 2,000 tons. The Asahi Denka Kogyo K. K. (Asahi Electro-Chemical Industry Co., Ltd.), Tokyo, is experimenting with its own process of electrolysing calcined magnesite, and the Nippon Soda K. K. (Japan Soda Co., Ltd.) Tokyo, also proposes a yearly production of 300 tons by the electrolysis of calcined magnesite.

This activity in the production of metallic magnesium in Japan is especially worthy of comment because of the general world interest in light alloys. For instance, in the report of the National Physical Laboratory for 1936 announcement is made of the development of two new groups of light magnesium alloys which are of special importance for the aircraft industry. The composition of one alloy in one of the series is 8.0 per cent. aluminium, 2.5 per cent. silver, 0.4 per cent. manganese, 0.2 per cent. calcium, with magnesium making up the balance.

Improving the Hardness of Pewter

IN a further contribution to the study of the mechanical properties of pewter, R. E. Leyman (*International Tin Research and Development Council*), three alloys of tin with antimony in the proportions of 3, 5 and 7 per cent. have been investigated without and with addition of either copper or silver in substitution of part of the tin. The copper additions (about 0.5, 1 and 3 per cent.) were made only to the 5 per cent. antimony alloy, while the silver was introduced in the same proportions in the 7 per cent. antimony alloy. Ingots of these compositions were reduced in thickness by repeated rolling, when the reduction per pass was about one per cent. Tests of Brinell hardness and examination of micrographic structure were made on specimens with reductions of from 10 to 80 per cent. All alloys were found to be hardened by moderate cold rolling down to 40 or 50 per cent.; further rolling softened them, the softening becoming more pronounced with higher proportions of copper and silver. Annealing caused further softening in most cases, but some of the copper and silver alloys which had been severely worked improved slightly in hardness.

The Setting of Dental Amalgams

Constitution of Ternary Alloys of Silver, Tin and Mercury

THE correlation of results obtained during researches on the setting of amalgams (made from alloys of definite composition and under standardised conditions) with their constitution, as deduced from an examination of the silver-tin-mercury ternary system, was given in a paper which Dr. Marie L. V. Gayler read at a recent meeting of the Institute of Metals. This investigation formed part of a research carried out in the Department of Metallurgy of the National Physical Laboratory, on behalf of the Dental Investigation Committee of the Department of Scientific and Industrial Research, and with the aid of funds provided by the Dental Board of the United Kingdom.

It has long been known that if mercury be mixed with filings of silver-tin alloys, which have or have not been previously aged at 100° C., dimensional changes occur during the setting of the resultant amalgam. G. V. Black [1-3] (*circa* 1896) was the first to carry out researches on this problem.

Previous Researches

Gray, [4-10] Souder and Peters, [11, 12] Taylor, [13-15] Ward and Scott, [16] Rothen, [17] McBain and Knight, [18] Loebich [19,20] and Nowach, [21] Sterner-Rainer [22] have contributed largely to the knowledge of amalgams. Apart from the researches of Joyner, [23] and later of Knight and Joyner, [24] the constitution of the silver-tin-mercury alloys has not been studied and, therefore, explanations of this problem of the setting of amalgams have not been based on fundamental knowledge. Fenchel [25] photographed the structure of an amalgam at intervals up to 24 hrs. after mixing and thereby demonstrated the growth of crystals in an amalgam.

It has been shown [26] that dimensional changes during setting bear a definite relation to the composition of the dental alloys from which they are made. The microscopical examination of binary silver-tin alloys containing less than 25 per cent. tin, in the cast state, shows the presence of the β silver-tin phase embedded in a matrix of Ag_3Sn in an amount proportional to the percentage of tin present in the alloy, while that of alloys with 27 or more per cent. tin shows free tin and Ag_3Sn. If filings of such alloys are mixed with mercury under the conditions laid down and packed in a dental cavity, then amalgams made from alloys containing the lesser amount of tin will expand, while those with the greater amount will contract on setting, the degree of expansion or contraction depending on the amount of β or free tin, respectively, in the alloys.

If up to 5 per cent. copper be added, replacing silver in Ag_3Sn, a general stiffening of the amalgam takes place, together with an increase in expansion (contraction being considered as negative expansion). Alloys giving amalgams which expand on setting contain less than 25 per cent. tin, and those which contract, more than 27 per cent. tin.

Theory of the Setting Process

Excess of tin in the dental alloy is to be condemned, since it causes the formation of the γ_2 constituent; on the other hand, an insufficient amount of tin in the alloy increases the amount of the γ_1 silver-mercury compound formed, which results in expansion. Therefore the composition of an amalgam which shall neither expand nor contract must lie, under ideal conditions, at the junction of the four phase fields, β_1, $\beta_1 + \gamma_1$, $\beta_1 + \gamma_1 + \gamma_2$, $\beta_1 + \gamma_2$.

Fenchel [30] found that the combination of Ag_3Sn and mercury takes place with marked contraction. Knight and Joyner [24] from a restricted study of the equilibrium of silver-tin-mercury alloys at room temperature to about 214° C., concluded that amalgamation might be summed up as:—

$$Ag_3Sn + 4\ Hg \rightarrow Ag_3Hg_4 + Sn.$$

McBain and Knight [31] in an extension of this research found "that in the presence of mercury the tin and the silver in the alloy undergoing amalgamation cannot be combined with one another in any way, and therefore the products of amalgamation are the same as if each metal had been amalgamated separately . . . the alloy, which is a mechanical mixture of the compound Ag_3Sn and tin, becomes a mixture of *Arbor Dianæ* and tin." They found, also, that the addition of mercury to Ag_3Sn resulted in marked contraction whether the filings were previously aged at 100° C. or not; they remark that "every case occurring in dental practice must be intermediate between no volume change and the extreme changes mentioned above. This will depend on how nearly the amalgamation is complete before insertion."

Gray, [8 10] explained the peculiar alternation of contractions and expansions which take place in amalgams (when made in a specified manner) by a theory based on the work of McBain, Joyner, and Knight, supplemented by his own observations and general physico-chemical facts: "(*a*) The rapid drop to a minimum that forms the first part of the typical curve of reaction expansion evidently represents the end of the stage dominated by contraction accompanying solution of the alloy in mercury and formation of compounds with silver and copper. (*b*) Crystallisation of these mercury compounds quickly follows their formation, and is accompanied by expansion. The first minimum in the curve marks the time when the rapidity of this expansion just equals the rapidity of the contraction caused by the simultaneous formation of more of these same compounds. (*c*) As the solution and reaction diminish, the crystallisation expansion comes to predominate. This predominance is indicated by the rise of the curve from the first minimum to the first maximum."

A Complex Reaction

Gray accepts McBain's and Joyner's conclusions with regard to the process of amalgamation, *viz.*,

$$Ag_3Sn + Hg \rightarrow Ag_3Hg_4 + Sn.$$

The theory put forward by Dr. Gayler is based on (1) a knowledge of the constitution of the alloys of silver, tin, and mercury; (2) observations on the behaviour of alloys and mercury during mixing; and (3) X-ray analysis of dental alloys and amalgams. It has already been shown in the paper on the constitution of the ternary alloys [29] that the effect of the additions of mercury to Ag_3Sn cannot be summed up by the simple equation

$$Ag_3Sn + 4\ Hg \rightarrow Ag_3Hg_4 + Sn$$

A very much more complex reaction takes place.

The addition of up to 64 per cent. mercury to Ag_3Sn results in the formation of three phases in proportions depending on the constitution of the alloy: (*a*) The β phase of the silver-tin system, in which mercury is held in solid solution, forms a continuous series of solid solutions with the β_1 phase of the silver-mercury system in which tin is held in solid solution. These two phases are therefore isomorphous and form a series of solid solutions (which have been designated β_1), which stretch right across the ternary diagram. (*b*) The γ_1 phase of the silver-mercury system which contains a small amount of tin in solid solution. (*c*) The γ_2 phase of the tin-mercury system.

If Ag_3Sn and not more than 64 per cent. mercury are mixed together at some temperature above 150° C., and then cooled to mouth temperature, the following reactions take place:—

(i) Ag_3Sn + liq. Hg $\rightarrow$ β_1 + liquid (at 150° C.);

(ii) As the temperature falls the γ_2 phase separates from the mixture, β_1 + liquid, until the temperature of 84° C. is reached. Here, from the residual β_1 and liquid, the $\gamma_1 + \gamma_2$ phases separate according to the following equation

$$\beta_1 + \text{liq.} \rightarrow \gamma_1 + \gamma_2.$$

Alloys in equilibrium containing less than 65 per cent. mercury will, therefore, be completely solid below 84° C. and will consist of $\beta_1 + \gamma_2$ from 15 to 18 per cent. mercury, and

of $\beta_1 + \gamma_1 + \gamma_2$ from 18 to 65 per cent. mercury. Excess mercury, above 65 per cent., results in additional complex reactions as shown on examining the diagram mentioned above.

The changes taking place when mercury is mixed with Ag_3Sn cannot, therefore, be summed up by a simple equation; under equilibrium conditions the resulting product of amalgamation at temperatures below 70° C. consists of a mixture of the β_1 and γ_2 phases with or without the γ_1 phase, depending on the amount of mercury used. In the case of dental amalgams, the degree of amalgamation varies with the method of mixing and therefore the final constitution of the resulting amalgam will depend on factors connected with mixing and subsequent manipulation.

Steps in Transformation

It has been found [28] that an alloy of satisfactory composition should be mixed with mercury in the ratio 1 :1.75 which corresponds with 63.6 per cent. mercury. In the case of alloys in which copper replaces up to 5 per cent. of silver in the compound Ag_3Sn, this particular ratio will give an alloy which is identical with that of the invariant point, at 84° C., given by the equation

$$\beta_1 + \text{liq.} \rightarrow \gamma_1 + \gamma^2.$$

Therefore the transformation of Ag_3Sn into, ultimately, $\gamma_1 + \gamma^2$, should proceed at a maximum rate at room temperature when the amount of mercury used is 64 per cent.

It is highly probable that the first step in the transformation of Ag_3Sn will be the formation of a solid solution of mercury in Ag_3Sn and then the formation of $\beta_1 + \gamma_2$ on the outside of the particles; the amount formed will depend on the rate of the diffusion of mercury through the layer of $\beta_1 + \gamma_2$ which will decrease as the amount of these phases increases. If the particle size be large, or the amount of mercury insufficient, a core of Ag_3Sn may be left surrounded with $\beta_1 + \gamma_2$. These constituents will react with the adjoining mercury as soon as they are formed to give $\gamma_1 + \gamma_2$, thereby inhibiting the diffusion of mercury and preventing further transformation of Ag_3Sn. The quantity of γ_2 formed simultaneously with γ_1 is necessarily relatively very little.

The proportions of the different phases which finally are formed in the amalgam will depend on (i) the composition of the dental alloy; (ii) the method of mixing and manipulation.

Effect of Particle Size

Particle size, as well as the composition of the dental alloy and the method of mixing, will have a marked effect on the setting of the resultant amalgam. If the particle size is very fine, the transformation of Ag_3Sn + mercury into $\gamma_1 + \gamma_2$ should proceed more nearly to completion, since diffusion will take place comparatively rapidly. If coarser particles of the same alloy are mixed with the same percentage of mercury, the reactions taking place on mixing will not proceed as far as in the above case. Most probably, after mixing, the amalgam will consist of small amounts of Ag_3Sn, β_1, γ_1, and γ_2, depending on the particular size. Expressing mercury reduces the content from 64 to 40-47 per cent. mercury, hence the subsequent reactions taking place will be different from those occurring when very fine particles of alloy are mixed.

If mercury is mixed with Ag_3Sn a marked contraction occurs; from the constitution of these alloys the first effect of the addition of mercury is the absorption of mercury and, possibly, the formation of the β_1 phase, from which $\beta_1 + \gamma_2 + \gamma_1$ are ultimately formed. If the dental alloy consists of Ag_3Sn + tin, the addition of mercury results in most complex changes taking place accompanied by a very rapid absorption of mercury. Dental alloys, containing less than 25 per cent. tin, when mixed with mercury, exhibit very marked expansion.

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Cupola Cokes

Foundry and Laboratory Characteristics

RESULTS from a series of tests on fourteen cupola cokes from various districts in Great Britain were recorded by H. O'Neil and J. G. Pearce in a paper read at the annual conference of the Institute of British Foundrymen, June, 1937. In one series each coke was used as bed and charge coke for a run of one day's duration, producing 60 tons of railway chairs from a 9 ton per hour cupola. In another series, eight of the cokes were used in a smaller cupola with very uniform and known charges, to determine their sulphur and carbon pick-up. In the third series a wide range of laboratory coke tests was undertaken, chemical, physical and structural, including analysis, wet oxidation, combustibility, reactivity, shatter, calorific value, porosity, compression strength, adaptability, macrostructure and microstructure. The main object in view was to see what correlation exists between cupola performance and laboratory tests, and to determine a practical order of merit.

The work reported in this paper appears to be the most elaborate yet undertaken on cupola coke, and was circulated to members of the British Cast Iron Research Association as their Bureau Report No. 164. It presents a mass of data carried out principally by the L.M.S. railway foundry and research laboratories and the British Cast Iron Research Association with the co-operation of the Northern Coke Research Committee and the Fuel Research Board.

The merit of the cokes was assessed on metal temperature, with a constant ratio of 16 to 1 of metal melted to coke in the charge. The temperatures varied from worst to best by almost 5 per cent. The most useful test for predicting the performance of a cupola coke proved to be the shatter test, and values below 80 are indicated as unsuitable for cupola purposes. More generally, cokes giving low metal temperatures are low in shatter, rate of wet oxidation, and resistance to abrasion, while cokes giving high metal temperatures are high in density and resistance to compression. Considering cokes in relation to their native coalfields, a decrease in temperature is associated with a decrease in shatter and rate of wet oxidation. The pick-up tests did not give the conclusive evidence hoped for as to a relation between sulphur pick-up, and combustible, as distinct from total sulphur.

Some Recent Metallurgical Patents

Steels for High Temperatures

STEEL alloys for use at high temperatures, particularly for the construction or lining of apparatus for treatment of materials with hydrogenating gases, or preheaters therefor, contain 0.06—0.3 per cent. of carbon, 1—4 per cent. of chromium, 0.1—2 per cent. of molybdenum, and 0.3—0.6 per cent. of tungsten, with or without up to 3 per cent. of nickel or up to 2 per cent. of vanadium, or both, and with usual amounts of silicon, manganese, copper, phosphorus, sulphur, titanium, and tantalum. (See Specification 461,251 of Johnson, G. W., I. G. Farbenindustrie).

Extraction of Precious Metals

IN a process for treating alkaline cyanide solution containing dissolved precious metals to effect precipitation of the same, an alkaline or alkaline earth bisulphite is treated with metallic zinc to form an alkaline or alkaline earth hydrosulphite which is an active reducing agent, the latter being introduced into the cyanide solution to deoxidise the latter and the zinc remaining from the first reaction acting as a precipitant. The solution is introduced into the cyanide solution which then flows through a precipitating filter and the filtrate is then oxidised to destroy any remaining reducing agent so that it can be used again. The zinc in the form of zinc dust may be mixed with the bisulphite to form an emulsion which is then added to the cyanide solution, and a lead salt which reacts with the bisulphite to form lead sulphite, may also be added to the emulsion. When zinc shavings are used instead of zinc dust, the addition of the lead salt is not required. (See Specification 461,252 of Merrill Co., Mills, L. D., Crowe, T. B., and Haun, J. C.

Removal of Sulphur from Steel

TO improve the eliminations of sulphur, steel is produced from the pig iron produced as described in Specification 460,138, in a basic Bessemer converter with a flux of burnt lime containing not more than 2.5 per cent. of silica. The amount of lime used is such that while the lime content of the slag is increased, the phosphoric acid content is not decreased below 18 per cent. To increase the absorptive power of the slag for sulphur, the temperature in the converter may be raised either by raising the temperature of the pig iron before charging into the converter, charging the lime into the hot converter before adding the pig iron, pre-heating or drying the air blast or by enriching the blast with oxygen. See Specification 461,958 of Brassert and Co., Ltd., H. A., Brassert, H. A., and Colclough, T. P.).

Annealing Aluminium Alloys

IN a heat-treated aluminium alloy containing magnesium silicide and copper, the content of magnesium silicide is at least 0.5 per cent. in excess of the amount soluble at the temperature of heat-treatment. The alloys may contain 1.5—3 per cent. of magnesium silicide and 0.1—4 per cent. of copper, with or without 0.1—1 per cent. of one or more of the metals chromium, molybdenum, tunsten, and uranium. The alloy is maintained at the temperature of heat-treatment, which may be between 500° C. and the temperature of incipient fusion, and is rapidly cooled, after which it may be aged for 3—36 hours at 140—200° C. (See Specification 463,324 of Alluminium, Ltd.).

Refining Metals with Iodine

MOLTEN metals and alloys are treated with iodine which is introduced in the form of crystals, preferably in a tube or container made of the metal or alloy under treatment. For example, brass for the production of wire, consisting of 61 per cent. of copper and 39 per cent. of zinc, may be made by melting the copper, adding the zinc and stirring, and introducing iodine crystals. The wire may afterwards be annealed in a halogen atmosphere. (See specification 461,756 of United Wire Works (Birmingham), Ltd., and Lowndes, H.

Sintered Iron Nickel Alloys

SINTERED iron-nickel alloys are made by reducing and sintering the oxides, the product obtained being subjected to cold working, optionally folowed by annealing and further cold working. The oxides may be reduced separately and then mixed and sintered, or the oxides may be mixed and reduced together and then sintered. A single cold working with a change of shape of 90 per cent. or more may be applied, or the change of shape may be of less extent followed by annealing at about 1,000° C., a second cold working with change of shape of about 50 per cent., and a final annealing at about 400° C. (See Specification 461,948 of Siemens and Halske Akt.-Ges.

Cast Iron Alloy containing Copper

A CAST iron alloy is made by adding 0.6 per cent. or more, preferably 1—3 per cent., of copper to a molten mixture containing at least 25 per cent. of steel, generally in the form of scrap steel, pig iron, and alloys. The copper may be added as the metal, alone or with a silicide of calcium, magnesium, or barium, or as an iron alloy containing 10—60 per cent. or more of copper, or a silicon alloy containing for example 30 per cent. or 70 per cent. of copper, or an alloy consisting of 76 per cent. of copper, 8 per cent. of calcium, and 16 per cent. of silicon. A graphitising agent is preferably added which may be any of the following: calcium, magnesium, barium, strontium, sodium, potassium, zirconium, titanium, beryllium, cerium, nickel, molybdenum, or silicides of these metals, or silicon, or ferro-silicon. (See Specification 463,145 of Meehanite Metal Corporation).

Sintered Hard Alloys

SINTERED hard alloys consist of 95—99 per cent. of tungsten carbide and 1—5 per cent. of one or more carbides which do not dissociate in contact with tungsten carbide at high temperatures, such as of tantalum, molybdenum, niobium, and titanium, there being no addition of low melting point metal. The alloys may be made by finely grinding the carbides together, pressing, and heating in a reducing atmosphere to 2100—2300° C. (Specification 463,239 of British Thomson-Houston Co., Ltd.).

Nickel Alloys

Nickel or nickel alloys are rendered devoid of commercial "red shortness" by ascertaining the amounts of one or more of the elements titanium, zirconium, boron, phosphorus, and arsenic that is necessary to render the resultant alloy devoid of commercial "red shortness" and then adding to the molten nickel, etc., a restricted controlled amount of the element or elements referred to above in accordance with the figure ascertained. In carrying out the process, a small amount of the elements referred to above is added, and the malleability at elevated temperature of a specimen obtained from the mass, the procedure being repeated if necessary until a specimen is obtained which is not commercially "red short" and the mass then cast. The malleability is ascertained by forming a test piece and then subjecting it to the "hammer and anvil test." The malleabilising agent used may be either titanium or zirconium together with either prosphorus or boron or arsenic, and these elements may be used in association with one or more deoxidising or like agents such as magnesium or aluminium. The molten nickel, etc., may be treated with either titanium or zirconium, then magnesium and then either boron or phosphorus, and also with aluminium before the treatment with titanium, etc. Examples of malleabilising agents used are 0.01 per cent. of boron or 0.05 of titanium in conjunction with 0.15 of phosphorus or 0.01 of boron for nickel copper alloys, or 0.01 of zirconium in conjunction with 0.005—0.15 of phosphorus or 0.003—0.02 of boron especially when used in conjunction with 0.05—0.2 of aluminium or 0.02—0.15 of magnesium. (See specification 459,431 of Monk Nickel Co., Ltd.).

Iron and Steel Institute

Grants from Andrew Carnegie Research Fund

THE Council of the Iron and Steel Institute are prepared to make annually a limited number of grants from the research fund founded by the late Mr. Andrew Carnegie in aid of metallurgical research work.

The object of the scheme is not to facilitate ordinary collegiate studies, but to enable students, who have passed through a college curriculum or have been trained in industrial establishments, to conduct researches on problems of practical and scientific importance relating to the metallurgy of iron and steel and allied subjects. Candidates, who must be under 35 years of age, must apply before September 30, on a special form to be obtained from the Secretary of the Institute.

The value of the grant will depend on the nature of the proposed research work, but the maximum amount granted in any one year will, as a rule, not exceed £100.

The results of the research shall be communicated to the Iron and Steel Institute, which will have the right of priority of publication in full, and will bear the whole costs thereof.

Cadmium in Tin-Rich Alloys

Separation by Process of Volatilisation

THE volatilisation of cadmium from alloys rich in tin can be made so complete without appreciable loss of tin that it has been adopted as a method of analysis. The procedure which Professor D. Hanson and Dr. W. T. Pell-Walpole have developed during their investigations on the constitution of alloys of cadmium and antimony with tin is described in Technical Publications, Ser. A., No. 55, of the International Tin Research and Development Council.

The separation of the tin and cadmium depends on the high volatility of cadmium compared with that of tin: thus, at atmospheric pressure pure cadmium boils at 760° C., whilst the vapour pressure of tin at this temperature is of the order of 10^{-5} mm. of mercury. Some preliminary experiments showed that the cadmium can be removed completely from a mechanical mixture of 2 gram of tin with 2 gram of cadmium, if the mixture is maintained *in vacuo* (0.03 m.m. of mercury) at 700° C. for 20 minutes. Similarly the cadmium is completely removed by volatilisation from a 4 gram sample of an alloy consisting of 50 per cent. of cadmium and 50 per cent. of tin.

The procedure finally adopted was as follows: Two 3 gram samples of the alloy are weighed into porcelain combustion boats, which are placed in a silica tube closed at one end and connected to a vacuum pump at the other end. The tube is then evacuated and placed in a horizontal furnace kept at 700° to 730° C. If the tube is allowed to project some distance from the end of the furnace, the rubber bung which carries the tube leading to the pump is kept cool. A simple trap is placed between the silica tube and the pump.

The silica tube becomes heated to the temperature of the furnace within a few minutes and is left in the furnace for a total time of 30 minutes, continuous pumping being maintained to draw the cadmium vapour to the cooler parts of the system. The evacuated tube is then removed from the furnace and allowed to cool to a temperature below the melting-point of pure tin, before air is admitted. The samples are then removed and weighed, the loss of weight being taken as the cadmium content. A high vacuum is not necessary, since it was found that a hand-pump giving a vacuum of 1 mm. of mercury was quite as satisfactory as a high vacuum pump which reduced the pressure to 0.03 mm. of mercury. In either case the residual button of tin has a very bright untarnished appearance.

Several check analyses may be carried out simultaneously, and different alloys also may be treated at the same time, but it is advisable to use combustion boats of porcelain or some similar impervious material due to the very high fluidity and penetrating power of molten tin at high temperatures. Ordinary fireclay combustion boats will only serve for a few heats. Blank estimations on samples of Chempur tin gave the following results:

No.	Change in Weight per cent.
1	+0.016
2	0.000
3	−0.015
4	0.000

The variations obtained on repeated determinations of 23 different cadmium-tin alloys are shown tabulated in the publication to which reference has been made.

This method has since been applied successfully to the determination of cadmium in tin-rich antimony-cadmium-tin alloys. A blank determination was made first on an antimony-tin alloy containing no cadmium. A specimen containing 14 per cent. of antimony was chosen and this was heated for 30 minutes in a vacuum of 0.03 mm. of mercury at 780° C. No loss of weight was recorded, hence it was concluded that antimony would not interfere with the determination of cadmium in tin-rich alloys by the volatilisation method, since the temperature used for this experiment is 50° C. higher than is necessary for the complete removal of cadmium from tin. A further check was obtained by volumetric determination of the antimony content of several alloys before and after the removal of the cadmium by volatilisation.

Non-Ferrous Metals Research

Creep Characteristics

IT has long been recognised that metals undergo slow deformation or creep when subjected for prolonged periods to high temperatures and stresses, but systematic investigations of the phenomenon have been conducted only in comparatively recent years. At the present time extensive studies of the creep characteristics of materials are in progress, and engineers are adopting the data obtained, as a basis for design, in place of those derived from tests of short duration.

In their Research Report R.R.A. 449 ("Creep of Non-Ferrous Metals and Alloys: a Review of Published Information," by W. A. Baker) the British Non-Ferrous Metals Research Association summarises the available published information relating to the creep characteristics of non-ferrous metals and alloys. The data presented have been selected critically, and include information on copper and copper alloys, nickel alloys, aluminium and aluminium alloys, and lead. The numerical values are set out in tabular form convenient for reference, with compositions of materials.

Fatigue Resistance of Lead Alloys

For a number of years past the British Non-Ferrous Metals Research Association have also been investigating the properties of lead and lead alloys in relation to their use for cable sheathing, water piping and rolled sheet. In the course of this work extensive information on the fatigue resistance of lead and lead alloys has been obtained. These results, hitherto available in a large numver of separate reports mainly issued to members of the association only, are now collected and tabulated in Research Report R.R.A. 440 ("The Fatigue Resistance of Lead and Lead Alloys," by H. Waterhouse).

The materials covered include lead in various conditions and degrees of purity, and lead with small additions of, respectively, tin, antimony, cadmium, calcium, barium, copper, nickel, and bismuth; tin plus cadmium, antimony plus cadmium, tin plus antimony, tin plus cadmium plus copper, antimony plus cadmium plus copper, and bismuth plus magnesium. In addition a few results of tests conducted at 100° C. in air are given as well as some selected results showing the effects of surrounding media and protective coatings on the fatigue resistance of lead and lead alloys.

These reports are obtainable from the association at Regnart Buildings, Euston Street, London, N.W.1 (price 2s. each, post free).

Metallurgical Section

October 2, 1937

Metal Extraction and Mining Developments

Although Germany increased its aluminium production from 18,900 tons in 1933 to 95,200 in 1936, the home requirements have not yet been fulfilled, although it is hoped that production will have attained adequate levels by the end of 1937. The 1936 annual report of the Vereinigte Aluminium Werke of Lautawerk, which is a Government-owned concern supplying about 75 per cent. of the national aluminium output, emphasises the importance of new and improved alloys, especially silumin, in the extension of uses for aluminium. Compared with exports, German imports of aluminium are small. The outstanding characteristic of the export trade since 1933 has been the steady gain recorded for finished aluminium products. Exports of all aluminium products totalled 14,177 tons in 1936, and have been 4,341 tons for the first four months of 1937.

The Th. Goldschmidt of Essen, an important chemico-metallurgical concern, has announced the completion of arrangements with the Vereinigte Aluminium Werke for the establishment of a large plant to utilise low-grade German alumina clays. In Czechoslovakia plans are being formed by the Eisenbahngesellschaft der Ferdinands Nordbahn for the production of aluminium, as many bauxite deposits have been found.

The profitable production of relatively low-grade copper ores in British Columbia is now dependent on present world prices for copper. The Granby Mining and Smelting Co., one of the two large British Columbia producers, accumulated large stocks of unsold copper during the depression and discontinued mining operations late in 1935, thereby accounting for the decline in copper output from 48,085,000 lb. in 1934, 38,791,000 lb. in 1935, to 20,807,000 lb. in 1936. The Granby mine at Allenby was reopened in June, 1937, and other concerns have also resumed full-time operations. It is understood that the entire copper output of the Granby Mining and Smelting Co. is under contract for the next three years to Japanese interests.

In Czechoslovakia the Montania Mining and Smelting Co., of Bratislava, is to reopen the copper mines at Henzlova, Mbisk, and Svedlary, which were in operation over 100 years and closed in 1933. When in operation, these mines produced about 10,000 tons of concentrates annually, which were exported to German smelters. Germany's expansion of its copper smelting industry, based upon foreign copper ore and raw metal, is revealed by the increased gross operating income and dividends of the Norddeutsche Affinerie, Hamburg, the leading German smelter. This company recently enlarged and modernised its refinery and constructed a new reverberatory furnace for smelting copper concentrates. A new sulphuric acid plant using the contact process and the enlargement of the roasting plant were completed in September, 1936. The size of the smelter can be gauged from the fact that 1,356 men were employed at the end of 1936. German imports of copper ores and concentrates totalled 179,061 tons for the first 4 months of 1937, compared with 145,306 tons for the same period in 1936.

In the Union of South Africa, Parliament has made provisions for assisting the O'okiep Copper Co., recently formed to exploit the copper deposits in Namaqualand. This company is under the control of the South African Copper Co., Ltd., incorporated in the United States in 1928, and the American Metal Corporation are financially interested. The new enterprise plans to erect concentrating and refining plants at the mine, instead of exporting the product to Wales for refining. An initial annual output of 20,000 tons is anticipated. Installation of the new machinery should be complete, and operations started, early in 1939.

German imports of manganese ore have leaped ahead during 1937, 146,920 tons having been imported during the first 4 months of the year, compared with 65,404 tons for the same period in 1936. Increased quantities are now coming from British South Africa, British India, Brazil, and Hungary, while the U.S.S.R. is furnishing negligible amounts. Germany has also increased its own output of low-grade manganese ore, and special concentrating methods have been installed for the manganese. The 1936 output is estimated at 3,000,000 tons of ore carrying less than 12 per cent. manganese, 200,000 tons of 12 to 30 per cent. manganese, and only 300 tons with more than 30 per cent. manganese. Imported ores, however, generally contain considerably more than 30 per cent. of manganese. Among new processes to replace the consumption of manganese is one developed by the Volklinger Huttenwerk, in the Saar district, which uses sodium carbonate to remove sulphur from raw iron made from low-grade southern German iron ore. Only 1 to 2 per cent. of soda is required for this desulphurisation, formerly accomplished with manganese ore.

The persistent demand and high price obtainable for tantalite have caused increased mining activity near Darwin, Northern Territory, Australia. About 600 lb. recovered in 1936, and a similar quantity found during the first half of 1937, were shipped to America. It is reported, however, that chemical interests in Hamburg are prepared to purchase all tantalite produced; Japanese users are also interested in obtaining supplies. The tantalite is being used to harden steel.

De-Tinning Practice in Germany

AUTHENTIC data on the output of tin metal in Germany is lacking, but production in 1936 is estimated to have been about 7,000 tons, compared with 6,500 tons in 1935. A considerable contraction in the consumption of tin doubtless occurred in 1936 as a result of the vigorous efforts which were and are still

being made to dispense with imported metal as much as possible, and the possible decreased consumption as estimated is indicated by a considerable drop in the surplus of imports over exports from 11,000 in 1935, to 8,470 tons in 1936, a decrease which is considerably larger than the estimated gain in domestic production.

Increased activity of the German tin-smelting industry is shown by the further rise in imports of tin ore, following a considerable expansion in preceding years from 600 tons in 1934, to 1,230 tons in 1935, and 1,560 tons in 1936. This imported ore, however, furnishes only a relatively small part of the German output of tin metal; the greater part is being recovered by detinning cans and tin-containing residues. In 1935 the metal recovered by detinning supplied 56 per cent. of the tin output, old and scrap metal supplied 25 per cent., and ores only 19 per cent. In 1935 there were in operation in Germany two tin smelters and four de-tinning plants, and also two other plants where tin oxide and tin-containing ashes and residues were smelted exclusively. Output of the tin smelters and de-tinning plants amounted to 5,960 tons of tin metal in 1935, compared with 5,900 tons in 1936. Of the 1935 output, 2,075 tons consisted of pure tin and 3,885 tons was mixed-tin and other tin alloys.

De-tinning Processes Employed

The present-day processes which are successfully used in de-tinning are mainly improvements upon abandoned processes of the past seventy-five years, during which period a very large number of patents have been granted for the recovery of tin metal from scrap tinplate. In the electrolytic process a 70 per cent. solution of caustic soda, heated to 70° C., is the usual electrolyte, but acid processes are also in use. With the alkaline electrolyte, any oil, grease, paint or varnish on the scrap is converted into a soap by the action of the caustic soda, and this soap dissolves in the bath, where—to some extent—it preserves the spongy tin from oxidation when taken from the bath. Complete stripping, however, is not always obtained, but there is great advantage in recovering the tin direct in the metallic state whilst the average cost of power is about 100 k.w.h. per ton of scrap treated.

Chlorine is the agent employed in the dry chemical process, by which 75 per cent. of the world's tin scrap is treated. The first patent for this process was taken out in 1850, but it was not until 1905 that the process became commercially successful, through the efforts of Goldschmidt and the coming of cheap supplies of chlorine gas. By this process the scrap can be treated in large quantities, the residual scrap leaves the plant in a well stripped condition, and the stannic chloride (which is the recovered product) is pure and is a product for which there is a demand. From 80 to 100 lb. of chlorine is used per ton of scrap treated. The cost of treatment is about equal to the value of the de-tinned scrap, but the initial cost of the plant may be as much as £16,000 for a capacity of 200 tons of scrap per week. Oil, grease, paint and varnish must be removed before the scrap is submitted to the action of the chlorine, and rigid temperature control is essential to prevent the chlorine from subsequently attacking the iron as the heat formation of stannic chloride is high and the temperature of the mass could easily rise to incandescence.

Successful wet chemical processes depend on the use of caustic soda as solvent, the reaction being speeded up by the addition of oxidising agents as a boiling solution of caustic soda used alone would require over two days to effect the dissolving of the tin. The use of an alkaline solution of litharge, patented in 1884, was used on a large scale in Germany in 1890, but fell into disrepute as the electrolytic process increased in popularity. It was again patented in the United States in 1911 by Ramage, the tin being separated from the sodium stannate by the addition of scrap galvanised iron. Alkaline solutions of chromate, nitrite, sodium nitrate, sodium chloride, and manganese dioxide have also been proposed.

Vanadium Steels and Irons

The uses and advantages of vanadium in connection with ferrous metallurgy are discussed in an informative manner in a book recently published by the Vanadium Corporation of America. The two main characteristics, which are caused by the addition of vanadium to any steel, i.e., the reduction of the inherent grain size and the reduction in the size of the carbides, are illustrated by a series of photo-micrographs. Vanadium has also a distinct effect on the behaviour of a steel on quenching. The vanadium carbides are relatively stable and dissolve more slowly than the iron carbides, even at temperatures well above those used in ordinary heat treatment. In consequence of this, the use of quenching temperatures that cause little or no vanadium carbide to go into solution, give rise to exceptional combinations of strength and toughness. Using quenching temperatures sufficiently high partly to dissolve the vanadium carbides, an increased depth of hardening may be obtained without sacrificing the advantages of fine grain, and this hardness is retained to higher temperatures than with plain carbon steel.

The chrome vanadium steels, as used extensively in America, contain chromium 0.80—1.10 per cent., vanadium 0.15—0.20 per cent., and carbon increasing from 0.10 to 1.0 per cent. The low carbon steels, in addition to their well-known use for case-hardened engine parts are being utilised increasingly for welded pressure vessels. The usual method of fabrication is electric arc-welding with heavily-coated chromium vanadium electrodes, followed by either full annealing or usually merely tempering for stress-relieving purposes. Exhaustive data on the types of plates used for this purpose is given in the above-mentioned book. Much information is also given concerning two steels containing 1.20 and 1.75 per cent. manganese and 0.15 vanadium. These steels combine a high yield point with high ductility, while they are usually resistant to fatigue. They have also a high resistance to impact, not only at ordinary temperatures, but down to −75° F. They are being used for rivets, etc., welded tanks and transportation units. It is stated that during the last ten years all high class American steelmakers are manufacturers of heavy forgings have been using 0.05 to 0.20 per cent. vanadium, with full addition of silicon and minimum use of aluminium to eliminate ghost lines and control grain size. The addition of vanadium to cast steels has been widely used to obtain improved mechanical properties. The principal advantage in general is the increased elastic ratio and higher impact strength and wear resistance without any decrease in the ductility in tension.

Recent Progress in Non-Ferrous Metallurgy

Annual Autumn Meeting of the Institute of Metals

THE 29th annual autumn meeting of the Institute of Metals was held in Sheffield, September 6-9, by invitation of the local section of the Institute and with the co-operation of the industrialists of Sheffield and the University of Sheffield. The arrangements were made by a reception committee of which the chairman was Professor J. H. Andrew, D.Sc., and the honorary secretary was Mr. E. J. Thackeray.

The meeting began with a reception of members and their ladies by the Lord Mayor of Sheffield (Councillor Mrs. A. E. Longden, J.P.), the senior Pro-Chancellor (Lieut.-Colonel Sir H. K. Stephenson), of the University of Sheffield, and the president of the Institute of Metals (Mr. W. R. Barclay). At a business meeting which took place the following officers were nominated for 1938-39:—President, Dr. C. H. Desch; vice-president, Professor J. H. Andrew; members of council, Dr. J. W. Donaldson, Engineer Vice-Admiral G. Preece, and Mr. H. S. Tasker.

The 16th autumn lecture on "Metallurgy and the Aero Engine" was delivered by Dr. D. R. Pye, F.R.S., director of scientific research, Air Ministry.

Visits were made to the works of United Steel Companies, Ltd., English Steel Corporation, Ltd., Brown Bayley's Steel Works, Ltd., Mellows and Co., Ltd. Thos. Firth and John Brown, Ltd., Edgar Allen and Co., Ltd., Hadfields, Ltd., and Walker and Hall, Ltd.

On the evening of September 7 a civic reception and dance was given at the Town Hall by the Lord Mayor of Sheffield. On September 8 members and their ladies were entertained at a banquet and dance at the Royal Victoria Station Hotel. The final day of the meeting was devoted to a whole-day motor excursion in Derbyshire.

Metallurgy and the Aero Engine

The problems which concern the metallurgist are broadly classed as thermal and mechanical, said Dr. Pye in his lecture on "Metallurgy and the Aero Engine." On the thermal side it is fundamentally impossible to increase greatly the fraction of the heat generated which is turned into mechanical work. Therefore, 100 per cent. increase of power must involve an increase in the waste heat which has to be got rid of, in nearly the same proportion. A critical factor is always the piston which must be receiving about 40 per cent. more heat, and this has to be dissipated at the periphery via the piston rings and an oil film. Temperature observations on the piston are extremely difficult, but examination of the re-crystallisation of aluminium alloy pistons after use suggests that they may reach temperatures of 450° C. Any new material of about the same specific gravity and thermal conductivity which was better able to maintain its strength at temperatures of 300° C. and above would be of major importance.

The 100 per cent. increase of waste heat combined with the chemical problems introduced by the use of tetra-ethyl-lead in the fuel has profoundly affected the metallurgy of the exhaust valve. In spite of great improvements in steels, it is now necessary not only to transfer heat by convection away from the valve head by means of a hollow valve containing liquid, but also to coat the valve with special alloys to resist oxidation at the high temperatures involved. Sparking plugs are another critical factor, and their improvement involves interesting problems in which the engineer needs the help of the pure physicist.

On the mechanical side the chief metallurgical problem of the aero engine is that of maintaining two surfaces at high temperatures rubbing together without seizure. This is a problem firstly of lubrication, and hitherto it has been possible to rely safely upon an oil film to keep down the extent of the metallic contacts; but as the temperatures of the working surfaces increase, the viscosity of the oil gives less and less protection, and the nature of the metal surfaces themselves will play a more important role in the avoidance of seizure.

Surface Conditions and Seizure of Metals

Although working surfaces may be smooth, they are never flat, when considered in terms of molecular dimensions. They may be imagined as having the nature of a good golf green. As the humps in two heavy surfaces approach one another, a state of boundary lubrication is established, and as surface temperatures increase, the danger of incipient seizure is rendered greater. It is, therefore, of great importance to examine the possibility of treatment of the metallic surfaces themselves which will render them less liable to seizure. The line taken by the engineer to-day is to use one of the recognised methods of producing a hardened surface, but we do not know accurately in terms of ultimate atomic structure why one surface is hard and another soft. The problem of hardness and seizability must be studied in these terms, because seizure occurs by reason of automatic cohesions between the two surfaces.

Beilby showed 35 years ago that during the polishing process the normal crystalline structure of a metal surface is destroyed and the surface becomes amorphous, as though liquid metal had been smeared over the polished surface. This conclusion has been confirmed by the recent work of Finch and Bowden. It has also been shown that during the "running in" process always carried out before an engine is allowed to give its full load, a very thick Beilby layer of amorphous material is produced on the surface of a steel cylinder. Apart from the fact that observations have shown that a metal in the amorphous condition is harder and tougher than the crystalline variety, it is reasonable to suppose that an amorphous surface could be more easily protected from seizure by a thin oil film, than one of a crystalline character, of which the ultimate nature is a forest of minute peaks.

Such problems as these of the surface treatment of metals can only be successfully surmounted by the engineer with the advice of the physicist, and they are bound to assume a steadily greater importance where rubbing surfaces have to survive without seizure under high temperature conditions.

Determining Alumina mixed with Aluminium

A paper by G. B. Brook (chief chemist, The British Aluminium Co., Ltd., Kinlochleven) and A. G. Waddington (analytical chemist, The British Aluminium Co., Ltd., Kinlochleven) described an investigation into the volatilisation process for the determination of alumina in the presence of metallic aluminium, using hydrogen chloride. After reviewing the previous methods suggested for this determination, a description of a modified process and the required apparatus was given. The method has proved superior to any yet proposed for determining alumina in granulated aluminium dross, highly oxidised metal skimmings, etc. The complete separation of the metal as chloride and subsequent conversion to oxide allows the metallic content of the skimmings and dross to be accurately determined. The determination of inclusions such as cryolite and flux in metal is not possible, owing to the breakdown of the fluorides.

Investigations on the mechanical properties of carbon steels, copper, brasses, and aluminium alloys broken in tension at very high speeds were reported by D. W. Ginns, Engineering Laboratories, Cambridge University. The average time taken to reach the yield-point was 0.001 second, and to fracture 0.005 second. A pressure-resistance method was used for measuring stress, and a photo-cell method for strain, the two being combined to give a direct diagram on the cathode ray oscillograph. It was shown that, compared with the ordinary commercial tensile test values: (a) the yield-

point is increased very considerably, over 100 per cent. increase being recorded for some materials; (b) the maximum stress is increased by a much smaller amount; (c) the percentage elongation and the percentage reduction of area show comparatively small changes; (d) the types of fracture are almost identical with those obtained for the slow test.

Heat Treatment of Ni-Al-Cu Alloys

The effect of heat-treatment on hardness and electrical resistivity of copper-rich nickel-aluminium-copper alloys was reported by W. O. Alexander, research fellow, Metallurgy Department, University of Birmingham, and Professor D. Hanson, professor of metallurgy, University of Birmingham. Some 56 copper alloys, containing quantities of nickel and aluminium varying up to 10 per cent. by weight of each metal, were cast and extruded. The results indicate that above 800° C. all the alloys consist of uniform α solid solution. When heated at temperatures below 800° C. some of the alloys harden, and their electrical resistivity decreases. The results reveal the approximate limits of the α solid solution, while the manner of the changes in properties at lower temperatures implies precipitation of new phases, the origin of one lying in the direction of the nickel-aluminium binary system. The limit of α solid solubility is shown to decrease with decrease of temperature. Up to 8.5 per cent. of aluminium and 10 per cent. of nickel, which was the field of alloys investigated, α solid solution exists throughout the whole range at 800° C. and above. The greatest decrease in α solid solubility occurs over the temperature range 750° to 550° C. The limit of α solid solution at 400° C. and below is of the order of 1.5 per cent. nickel and 0.2 per cent. of aluminium. The disposition of alloys showing maximum hardening capacity together with minimum electrical resistivity agrees with the optimum ratio 4 : 1 nickel to aluminium suggested elsewhere. The origin of a separating phase lies in the direction of the nickel-aluminium binary system. The changes in electrical resistivity and hardness on annealing at lower temperatures of alloys quenched from 900° C. are similar to those occurring in other age-hardening systems.

A precision extensometer, reading by means of optical interference fringes to strains of 10^{-7} cm./cm., is used for creep experiments on tin was described by Bruce Chalmers, lecturer in physics and mathematics, Sir John Cass Technical Institute, London. The results were given under three headings: (*a*) single crystals; (*b*) specimens consisting of a few crystals with longitudinal crystal boundaries; and (*c*) specimens consisting of small crystals. They show that the change of orientation across a crystal boundary affects the mechanical properties of the boundary.

According to papers by J. L. Haughton, principal scientific officer, Metallurgy Department, National Physical Laboratory, Teddington, the constitution of magnesium-rich alloys of magnesium and calcium has been re-determined. The eutectic point occurs at 16.2 per cent. calcium and at 517° C.

Constitution of the Ni-Al System

The constitution of the nickel-aluminium system was the subject of a paper by W. O. Alexander, William Gibbins Fellow, Metallurgical Department, University of Birmingham, and N. B. Vaughan, British Non-Ferrous Metals Research Association, London. The system nickel-aluminium was studied by thermal and micrographic methods, and a hitherto unsuspected phase was found to exist, containing 84.5—87 per cent. nickel, and probably corresponding to the intermetallic compound Ni_3Al (86.7 per cent. nickel). Otherwise the diagram remains substantially as determined by Gwyer, except that the compound described by Gwyer as $NiAl_2$, is shown to be Ni_2Al_3. A change in solubility of nickel in NiAl causes alloys with 80—85 per cent. nickel to exhibit a suppressed structure when quenched from temperatures exceeding 1,150° C., and to undergo hardness changes on heat-treatment similar to those which occur in the suppressed β phase of the copper-aluminium system. Preliminary observations suggest that the nickel-rich alloys may possess desirable heat-resisting properties.

The deformation, on rolling, of alloys consisting of several phases having different yield-points, differs from that of alloys of homogeneous structure, according to a paper by Hermann Unckel, engineer for control and research, Finspongs Metallverk A.B., Finspong, Sweden. Harder particles embedded in a softer matrix deform less, and softer particles somewhat more, than the matrix. A secondary flow is thereby caused round the inclusions. Experiments with some two-phase alloys are described. It is shown that the deformation takes place in such a way that the work of deformation becomes a minimum value.

A paper by William Hume-Rothery, Royal Society Warren Research Fellow, Oxford, and Geoffrey Vincent Raynor, Keble College, Oxford, reported investigations on the equilibrium diagram of the system copper-gallium above 420° C. in the region 18—32 atomic per cent. gallium. Three distinct modifications of the β phase, denoted β, β', and β'', are shown to exist above 420° C., and there is evidence that a further modification exists at low temperatures. The β phase, stable at high temperature, has a considerable range of composition which diminishes rapidly with decreasing temperature until a eutectoid point is reached at 618° C. The phase boundaries for this modification of the β phase agree well with the diagram of Weibke, but, in contrast to the results of this investigator, the eutectoid transformation is not a reaction of the type $\beta \rightarrow \alpha + \gamma$, but $\beta \quad \beta' + \gamma$ where the β' phase exists over a narrow range of composition in the region 22.3 atomic per cent. gallium. The β' phase is stable above 475° C., at which temperature another transformation takes place with the formation of the β'' phase existing over a narrow range of composition in the region 21.5 atomic per cent. gallium.

Constitution and Properties of Sb-Cd-Sn Alloys

The constitution of antimony-cadmium-tin alloys containing up to 43 per cent. of cadmium and 14 per cent. of antimony has now been established by thermal and microscopical analyses. In a paper by Professor D. Hanson and W. T. Pell-Walpole, Department of Metallurgy, University of Birmingham, the results were presented as isothermal diagrams of the various surfaces, and as vertical and horizontal sections through the constitutional model. There are three ternary peritectic reactions at 227°, 209°, and 180° C., respectively. Metastable conditions occur during cooling in parts of the system, but these have been related to the stable state which is obtained by prolonged annealing of specimens. It is shown that at 227° C. tin will dissolve 9 per cent. of antimony with 1.5 per cent. of cadmium, and at 209° C. 5.5 per cent. of antimony with 2.4 per cent. of cadmium; below 209° C. the solubilities decrease continuously to 1 per cent. of antimony with 0.7 per cent. of cadmium at 148° C., and to 0.6 per cent. of each metal at 20° C. The solubility of antimony in the β phase of the cadmium-tin system decreases from 5.1 per cent. at 209° C. to 0.8 per cent. at 145° C.

A study of the mechanical properties of tin-rich antimony-cadmium-tin alloys was reported by Professor D. Hanson and W. T. Pell-Walpole, who investigated alloys containing up to 43 per cent. of cadmium and 14 per cent. of antimony in the form of annealed chill-cast specimens. Maximum stable values were obtained at a tensile strength of 7.0 tons per sq. in. and a Brinell hardness of 36. Tin-rich alloys containing 3 per cent. to 8 per cent. of cadmium with 9 per cent. of antimony were tested as rolled and after various heat-treatments. Two forms of hardening are obtained by quenching from suitable temperatures. One form is due to the solubility change of antimony in tin or in β; the other, which produces much more intense hardening, is analogous to the hardening of binary cadmium-tin alloys by quenching and depends on the suppression of the eutectoid decomposition of the β phase. Permanent improvement results in the first case, but the second type of hardening is only temporary, since complete self-annealing occurs at normal temperature (18° C.) within 18 months.

Fusible Alloys Containing Tin

A Number of Unusual Industrial Applications

MANY surprising applications of fusible alloys are described by E. J. Daniels, in Technical Publication, Series B, No. 5 of the International Tin Research and Development Council.

About one-half of this monograph is devoted to considering the bearing of composition upon the melting point and the structure and physical properties of the fusible alloys; the other half describes their applications. It is shown that Wood's metal, Lipowitz's alloy and other well-known compositions are extremely close approximations to the eutectic mixtures of phases consisting of either pure metals, solid solutions of one metal in another or intermetallic compounds. The microstructure is important since the strength and behaviour of the alloys depends on it. It is important to cast the alloys under controlled conditions to get dependable results, in regard to plasticity and creep. The solidification of many of these alloys is accompanied by expansion instead of contraction because they contain bismuth or antimony. The problems of corrosion of fusible alloys and methods of avoiding troubles due to this cause are discussed.

Amongst the applications given are sprinkler plugs, boiler plugs, fusible links, seals for glass apparatus, patterns for moulding and electroplating, tube bending, tempering baths and die-mounting.

The fact that alloys can be prepared which have melting-points approaching or even less than the boiling-point of water has long been known and has excited much interest, both from the metallurgical point of view in the relationship between composition and melting point, and from the practical point of view in the wide variety of uses to which these alloys may be put. The expression, "fusible metal," by which is meant easily melted *alloy*, is usually applied to alloys having melting-points below that of tin, excluding the amalgams or alloys containing mercury.

Relatively little is known of the relation between structure and mechanical properties of most of the low-melting alloys. The lead-tin, cadmium-tin, zinc-tin, cadmium-zinc, and tin-lead-bismuth eutectics have been shown to soften when cold-worked, whereas, of course, the usual structural materials, steel, copper, bronze, etc., are hardened by cold-work. Although bismuth, one of the principal constituents of the very fusible alloys, is commonly regarded as an extremely brittle metal, under suitable conditions it is capable of undergoing very considerable plastic deformation. Its plasticity, as determined by extrusion, lies between that of cadmium and tin. The mechanical properties of some lead and bismuth alloys in the cast condition which have been determined recently show that under fairly rapid straining, such as is used in the ordinary tensile test, the ternary and quaternary alloys containing bismuth (excluding the antimonial alloy) are reasonably ductile, giving quite large elongations.

Resistance to Corrosion

Very little information, also, is available on the resistance of the fusible alloys to corrosion. It appears that corrosion does not often occur but occasionally may prove serious. Thus, corrosion is stated to be an important cause of the failure to act of plugs for chlorine cylinders, and has been shown to affect seriously the reliability of boiler safety plugs. These boiler plugs are of bronze, threaded on the outside and filled with a tapered core of tin. They are screwed into the boiler at the lowest safe water level. Should the water drop below this, the plug, being exposed to the fire at its outer end and no longer cooled by the water at the other end, will become hot enough to melt the tin.

The fusible solder used in a sprinkler must have the necessary mechanical strength to hold the operating parts together until fire occurs. This necessitates a considerable margin between the operating temperature of the sprinkler and the normal temperature of its environment, since the strength of the solder and its resistance to creep fall very rapidly with rise in temperature and become very small before the melting-point is reached. It is for this reason that the use of Wood's metal gives the most sensitive sprinkler it is desirable to install in the average situation in a temperate climate. For tropical countries and in situations where industrial processes give out heat, such as in foundries, solders having a higher melting-point must be used.

Other Applications of Fusible Solder

Fusible solder is used also for a variety of other safety devices such as the releasing of automatic fire doors, the operation of alarms, etc. It is used for the protection of oil burner installations. In case of fire or abnormal rise of temperature, melting of a solder link causes valves to operate, shutting off the oil supply from the storage tank to the burner and so preventing a fire being fed with fuel from the tank. Fusible links are used for the protection of electric water-heater installations from excessive temperatures. The fuse link is called upon to retain its strength indefinitely at temperatures up to 90° C., and to melt and disconnect the electric supply at a safe temperature in the event of failure of the control thermostat.

Solders and seals are another application of the tin alloys with low melting-points. Any of the ternary or quaternary alloys may be used as solders, since they all contain a sufficient proportion of the metals which alloy with iron and copper, to ensure good adherence. The usual soft solders are made from tin and lead, to which a small proportion of antimony is occasionally added. For soldering aluminium, a mixture of tin with 40 to 50 per cent. zinc is often used. A low-melting solder for pewter consists of bismuth 50, tin 25 and lead 25 per cent.; others of slightly higher melting-point contain lead 50, tin 37.5 and bismuth 12.5 per cent. or tin 50, lead 25 and bismuth 25 per cent.

Fusible alloys in the molten condition have also been used to provide a gas-tight, non-inflammable liquid seal for industrial apparatus, such as large nitriding ovens.

Uses in Moulding

An interesting application of a fusible alloy is in the production of moulds or dies for the pressing of wood composition and fibre in order to imitate wood carvings. Cerromatrix, a bismuth-lead-tin alloy hardened with antimony, is used for this purpose. Its comparatively low melting-point allows it to be poured directly against the master wood carving without charring the wood, and it takes a sharp, clear-cut impression, showing every detail. The die so produced is sufficiently hard and rigid to withstand the pressure required in forming the plastic materials.

A modified Wood's metal, marketed under the name of Cerrobend and containing bismuth 50.0, tin 13.3, lead 26.7 and cadmium 10.0 per cent. is being used extensively for making master patterns for use with pantographic moulding and milling machines. Poured at the temperature of boiling water against wooden or plaster models, it gives a negative casting which is sufficiently hard to withstand the pressure of the "chaser" or follower of the machine, without wearing or crumbling, so that it lasts almost indefinitely and produces finished work of high accuracy.

Baths of the fusible alloys are suitable for tempering small steel tools. They are used by placing the article on the surface of the unmelted alloy, contained in some suitable vessel, and heating until fusion occurs. The article then falls below the surface, at which moment it is removed, having reached the correct temperature, and quickly cooled in water.

A cadmium-free fusible alloy hardened with antimony has recently been developed to replace the usual matrix alloys used for mounting dies and punches. It is marketed under the name Cerromatrix and contains bismuth 48.0, lead 28.5, tin 14.5, and antimony 9 per cent. Prior to the development of this alloy, antimonial lead, type metals, tin-lead solder, Wood's metal and sulphur were employed to a limited extent for die mounting but none of these materials proved to be entirely satisfactory. Antimonial lead, type metals and solder with their relatively high melting-temperatures tend to draw the die temper and their shrinkage during solidification causes loose fits. Wood's metal, although melting at a low temperature and not shrinking on solidification, is too soft, allowing the various parts of the die assembly to shift. The new matrix alloy melts at a sufficiently low temperature to obviate danger to the temper of the die, and expands slightly on solidification.

The low-melting metals and alloys are particularly suitable for the metallisation of wood. The dried wood is immersed in the molten metal or alloy in a suitable vessel which is at once closed and a mild pressure applied to the interior. The finished product consists of a wooden structure each of whose cells has an isolated charge of metal. Wooden blocks 16 in. by 4 in. by 2 in. are completely impregnated in a few seconds. The treatment can be controlled to give various degrees of penetration as required. The tensile strength of the wood is not affected, but hardness and compressive strength are notably increased.

Some Recent Metallurgical Patents

Magnesium and Magnesium Alloys

MAGNESIUM and magnesium alloys contaminated by calcium are refined by stirring the molten metal with a highly fluid flux consisting of or containing a substantial proportion of magnesium chloride, *e.g.*, carnallite, at temperatures below 900° C. and towards the end of the refining treatment adding to the mixture, while continuing the stirring, an inspissating agent such as a metal oxide and/or fluoride, *e.g.*, magnesium oxide and/or fluoride, in quantities sufficient to bring about thickening of the highly fluid flux. If, after the treatment above, it is desired to superheat the metal before pouring, the stirring is discontinued and the surface of the melt covered with a mixture of flux and inspissating agent. The melt is then superheated, cooled down to the pouring temperature and then cast. (See specification 459,912 of I. G. Farbenindustrie).

Extracting Precious Metals

IN a process for the recovery of precious metals from sweepings, residues, ores, concentrates, etc., the material is smelted under reducing conditions without the use of collector metals, the proportions of lime, iron and silicon present being so adjusted that easily fusible slags are formed, the lime content of which exceeds the ferrous oxide content; whereby it is ensured that the precious metals do not appreciably migrate into the slag. If excess of sulphur is present it may first be removed by an oxidising or sulphatising roast. Sweepings may be briquetted with binders such as lime or pitch. The crude product, which may consist for example of a silver-gold-platinum-copper alloy, may be worked up by usual methods. (See specification 457,902 of Deutsche Gold-und Silber Scheideanstalt Vorm. Roessler).

Manganese Alloys

MANGANESE ores or slags containing too large a proportion of iron to permit of being worked up to ferro-manganese in one stage are melted, after the addition if necessary of fluxes, *e.g.* limestone, fluorspar, or sand, to form a neutral or slightly acid and low-melting manganous oxide slag, and so much iron is reduced, as by means of charcoal, at a temperature below the reduction temperature of the manganese, as to form an intermediate product possessing an iron-manganese ratio required for producing the ferro-manganese desired. The basicity of this product is then increased by the addition of lime and on increase of temperature it is reduced to ferro-manganese. The two stages may be effected in one or separate furnaces. The iron reduced from the manganous oxide slag may be continuously or intermittently removed. In an example an ore containing 31.1 per cent. of iron and 17.8 per cent. of manganese are melted with a flux and by the addition of reducing charcoal so much iron is reduced at 1,300-1,400° C as to leave a manganous oxide slag containing 5.2 per cent. of iron and 25.9 per cent. of manganese. Lime and reducing charcoal are added to this slag which is reduced at about 1,600° C to ferro-manganese containing 11.4 per cent. of iron and 79.1 per cent. of manganese. (See Specification 454,165, of Mannesmann-Rohren-Werke and Sachtleben Akt.-Ges. Fur Bergbau und Chemische Industrie).

Hard Alloys

HARD alloys are produced by sintering together 91—94 per cent. of hard carbide, 5—7 per cent. of cobalt, 0.3—1.0 per cent. of tungsten and 0.5—2.0 per cent. of chromium with the addition of 0.05—0.2 per cent. of carbon; the hard carbide consists of one or more of tungsten carbide, molybdenum carbide, titanium carbide, and tantalum carbide. Carbon may be added in powder form, by sintering in a carbon-containing atmosphere, or by sintering in a carbon crucible or carbon tubular furnace. A powdered mixture of the components is pressed into the required form, preliminarily sintered at below 700° C., preferably at 500° C., brought into the required final form, and then sintered at a high temperature. (See Specification 461,872 of Siemens and Halske Akt.-Ges.

White Cast Iron Alloys

A WHITE cast iron having a melting-point between 1950 and 2010° F. and a Brinell hardness not less than 500 comprises 2—4 per cent. of carbon, not more than 2½ per cent. of silicon, not more than 1 per cent. of sulphur and 0.3 per cent. of phorphorus, and either 0.6—2.5 per cent. of boron or 0.2—2.5 per cent. of boron and 1.5—9 per cent. of nickel, the percentage amounts of boron and carbon in each case not exceeding 6. Manganese, chromium, tungsten, vanadium, molybdenum, and cobalt may be present. White cast iron comprising 2½—3½ per cent. of carbon, 0.75—1½ per cent. of boron, 2.5—6 per cent. of nickel, not over 1½ per cent. of silicon, and 0.05 per cent. each of sulphur and phosphorus is referred to. In making, the boron may be introduced in the form of aluminium-free ferro-boron of low sulphur and phosphorus content, or in the form of borax under which cast pig iron is melted in the presence of free carbons, *e.g.*, in a graphite crucible. (See Specification 462,284 of Triggs, W. W. (Industrial Research Laboratories, Ltd.).

Effect of Impurities in Copper

FOR a number of years past, the British Non-Ferrous Metals Research Association has been responsible for an investigation on the effects of various impurities on the properties of copper. The influence of numerous elements and combinations of elements was studied. The results of the research, which was carried out at the National Physical Laboratory, have hitherto been available only in a number of reports confidential to members of the Association, but are now to be generally released as one of the Association's Research Monographs, "Effect of Impurities in Copper," by S. L. Archbutt and W. E. Prytherch (price 12s. 6d.).

Metallurgical Section

November 6, 1937

Occlusion of Hydrogen by Nickel

The results of a new study on the occlusion and diffusion of hydrogen in metals, with particular reference to nickel (G. A. Moore and D. P. Smith, recently reported before the American Electrochemical Society), show that hydrogen enters the metal primarily along slip planes which are evidently rifted during rolling; that the large quantity of hydrogen taken up electrolytically, in excess of that which can be dissolved in the lattice, is retained chiefly in other rifts along planes of a family parallel to the plane of rolling; and that the latter rifts may have been present, at least in an incipient state, before the entry of hydrogen, and have been merely enlarged by the gas. Hydrogen patterns produced in nickel and in palladium are similar in type and it is considered that the differences found, which are due to the greater solubility of of hydrogen in the palladium than in the nickel lattice, do not necessarily require the assumption of changes different in kind from those which afford an adequate explanation of the effects found in nickel. In an earlier study metallographic methods were applied to the palladium-hydrogen system, and evidence was obtained that in rolled palladium a rapid preliminary distribution of electrolytic hydrogen takes place along planes of slip, preceding a slower general diffusion through the disordered lattice of the metal. Confirmation of the rôle of slip-plane crevices was found during a subsequent investigation of the rate of occlusion of gaseous hydrogen by recrystallised palladium. The present paper extends this study to the nickel-hydrogen system and compares the behaviour of nickel and palladium with reference to occlusion and diffusion.

From a consideration of the structures observed by present authors and others, it is considered probable that during rolling of nickel slip may occur, not only on the octahedral planes, but also on certain dodecahedral planes. The etching reagents used in the metallographic examination of both palladium and nickel were (1) a mixture of equal volumes of glacial acetic and concentrated nitric acids, specially valuable for removal of the Beilby layer, and (2) a saturated solution of chromic anhydride in concentrated nitric acid, which is peculiarly effective in developing hydrogen patterns.

Although Deville was the first to observe that certain metals, notably platinum, palladium and iron, became permeable to hydrogen at a red heat and therefrom concluded that "metals and alloys have a certain porosity," it was Graham (1866-69) who showed that the penetration could not be due to the porosity of the metal because hydrogen was the only gas which produced the phenomenon. Investigating the case of palladium, Trovsk and Hautefeuille (1874) concluded that a definite hydride of palladium was formed; Holt, Edgar and Firth (1913) suggested that the hydrogen existed partly as a condensed layer on the surface and partly dissolved in the interior of the metal. They found that palladium is normally inactive, but became active as a result of oxidation by heating in air and reduction of the oxide film in hydrogen; by heating to 400° in hydrogen, followed by cooling; and by heating to 400° *in vacuo*. The metal so activated soon lost its power of occlusion, and reheating became necessary. Most metals in a finely divided condition have now been found to absorb small quantities of hydrogen, and it has been observed that metals which are prepared by an electrolytic process will sometimes contain "occluded" hydrogen.

Wolfram Supplies

In view of the intensive demand for wolfram (tungsten ore) which became accentuated after the commencement of the rearmament programme, high prices have been a feature of the market; the price for August-September shipments was more than 25 per cent. higher than of the preceding month, and a three-fold increase by comparison with a year ago. With China responsible for about two-thirds of the world supplies, mined mainly in the four Southern provinces, there is great danger that the present hostilities in China will seriously interfere with supplies. This state of affairs, together with the high level of prices, however, may stimulate production in Bolivia, Burma, the Malay States and the United States, although it would be some time before these increased supplies could be made available. Ferro-tungsten is used as an alloy in steel for the production of the so-called "self-hardening" steels. It is associated with manganese in the once well-known Musket steel, although the use of chromium instead of manganese gives a better steel for heavy cutting work and Musket steel is now obsolete. These steels are incapable of being made soft by any known method, and are used particularly for high-speed cutting, in which the tool gets extremely hot but does not lose its cutting edge. An alloy of tungsten and carbon, with a few per cent. of cobalt, is known as Carboloy and yields one of the hardest known cutting edges for steel; it was discovered in 1926, and until then it was impossible to machine manganese steel.

Etching Reagents for Nickel Alloys

EXISTING data on metallurgical reagents are scattered widely to the great disadvantage of experimental workers in all fields of physical metallurgy. A very comprehensive and well arranged summary of the subjects, however, has recently been published in France under the title of "Etching Reagents for Use in Metallographic Investigation" (Paris: Dunod, 1937). The joint authors, A. Portevin and P. Bastien, make a preliminary survey of the means which have been employed to study the constituents of metallic materials, and discuss critically the significance and interpretation of patterns resulting from various treatments. Follow-

ing this introduction, a compendium of useful practical data relative to solutions, methods of use and results obtainable is presented in six chapters. There are reagents for use in photomicrographic examination of ferrous alloys; macrographic reagents for irons and steels; reagents for copper and copper alloys; for aluminium, magnesium and light metal alloys; tin, lead, cadmium, bismuth and bearing alloys; zinc and zinc alloys; nickel, chromium and their alloys; and for precious and refractory metals. Over two hundred etching treatments are described, and the accessibility of the information is further enhanced by the addition of tables in which the reagents are listed (1) by the names of the individuals to whom they owe their origin; (2) according to the metal or alloy to be examined; and (3) according to the main constituents of the solutions.

Corrosion of Metals in Soils

THE rate at which a metal pipe laid underground may be corroded by the soil is a matter of so much importance that the relative merits of the commonly-used ferrous materials—cast iron, wrought iron, and steel—has been a controversial question for many years. Dr. Scott Ewing, research associate of the American Gas Association, has now compared the composition of eight wrought ferrous materials used for soil corrosion tests at the United States National Bureau of Standards with the average pitting rate over a period of exposure of 12 years at 23 test sites, and he has drawn the conclusion that the only alloying element which appears to have any effect on the pitting rate is phosphorus. He finds that the pitting rate decreases slightly as the phosphorus content is increased up to about 0.1 per cent., and that this result is in rough accord with the results of atmospheric corrosion tests by the American Society for Testing Materials. Conditions in soils which cause the corrosion of lead and copper have also been considered. Lead, usually more resistant than the ferrous metals, was found to be pitted to a greater depth at six out of 47 test sites. In these six particular soils the sulphate content was very low and the soil was about neutral (pH 7) in reaction; lead is practically unaffected in soils containing large amounts of sulphates. Copper, in general, is more resistant than either lead or steel. It is seriously attacked in cinders; in soils containing relatively large amounts of chloride and carbonates the attack is appreciable but usually not serious. Heavy zinc (galvanised) coating gave good protection to steel pipes under the conditions of the tests, but lead-coated steel was pitted seriously; the reason for this difference is that zinc is " anodic " to steel, while lead is " cathodic."

Industrial Uses of Silver

FOLLOWING the publication of " Silver; Its Properties and Industrial Uses," by the United States National Bureau of Standards, October, 1936, a research project has been started by the American silver producers with the object of attacking this problem on a much broader front. Fifteen research fellows have been gathered together in nine different institutions, including the National Bureau of Standards, and are working on various phases of the problem. As the result of careful consideration the programme of research is to include studies of bactericidal, chemical, fungicidal, physico-chemical and thermal properties, as well as electro-plating, electrical characteristics, and metallurgical possibilities. The project, as a whole, will be co-ordinated from the National Bureau of Standards. Since the metallurgical field at present appears the most promising for new uses capable of absorbing a considerable part of the annual silver production, seven of the research fellows have been assigned metallurgical problems. The senior research associate, Mr. A. J. Dornblatt, formerly head of the metallurgy and chemistry section of the U.S. Naval Academy Post Graduate School, will act as the co-ordinating officer so that duplication of work among the different laboratories will be avoided. A considerable portion of his time will be spent contacting industry in order that commercial concerns may be interested in the work being done and to ensure that the scheme does not duplicate work which is already being carried on in industrial laboratories.

Problems being investigated include the effect of silver additions on the common engineering alloys, development of mechanically superior high silver alloys, characteristics of silver commutators, effects of silver in bearing metals, silver soldering irons, characteristics of welding rod containing silver, catalytic properties of silver, heat transfer data on silver and its alloys, optical reflectivity of silver alloys, effect of silver on spore germination, and electro-deposition of silver alloys. It is intended to publish progress reports from time to time. It is also desired and planned to co-operate with industry in following up suggestions regarding possible new industrial applications of silver.

Non-Metallic Elements in Steels

THE effects of non-metallic elements in steel were discussed by Mr. T. G. Bamford, in his recent presidential address to the Staffordshire Iron and Steel Institute. He mentioned that a number of practical experiments had recently been carried out by P. Bardenheuer, at the Kaiser Wilhelm Institute, Berlin, which proved conclusively what a devastating effect hydrogen could have upon the properties of steel. Plasticity could in part be restored by heating to a red heat, at which temperature ionisation of gas in the metal took place to an appreciable extent and the gas diffused slowly through the metal, escaping into the surrounding atmosphere. Speaking of nitride formation, he pointed out that it is well known that nitrogen is more readily absorbed if the metal is heated in ammonia, which decomposes at the metal surface, but since the process is essentially one of nitride formation and not simple diffusion of the atomic nitrogen, it follows that, when a layer of the nitride, Fe_2N, has formed on the surface of the metal, the rate at which nitrogen penetrates further is governed by the rate with which the solid phases react and not by the composition of the gas enveloping it. Thus Fisher and Shaw had shown recently that the presence of 80 per cent. of nitrogen in the gas does not impair the efficiency of the nitriding process. Dilution of the ammonia with hydrogen reduces the depth of case, but after the nitride surface layer has been formed, by even a few minutes' treatment in ammonia, a dilution with one-third its volume of hydrogen has no effect. Larger additions of hydrogen reverse the nitriding process, the nitrides being decomposed with formation of ammonia which passes away in the gas stream.

British Cast Iron Research Association

Work of the Sub-Committees, 1936-37

GREY iron and nickel and alloy cast irons continue to engage the attention of the Sub-Committees of the British Cast Iron Research Association, according to the 16th annual report, 1936-37. The work reported last year on graphite refinement, by means of which the highest possible degree of graphite refinement is secured, has been followed along several lines. Attempts have been made to apply the process to the cupola furnace, for which purpose a small experimental cupola was built. This problem has proved to be extremely difficult and the conditions leading to refinement from the cupola are not yet fully established, although definite progress has been made. In view of the strong theoretical possibility referred to in the last report that the change is associated with the presence in the melt of non-metallic inclusions, considerable work has been done on the separation and analysis of inclusions in both pig and cast iron.

Separation and Analysis of Inclusions

The first separation method adopted was the alcoholic iodine method recommended by the Oxygen Panel of the Iron and Steel Institute's Ingot Committee. In addition, the apparatus for the chlorine method has been set up. In view of its difficulty and delicacy this work is being carried out in close conjunction with other laboratories in the country, working on the same problem, through the Oxygen Panel, and attention is being given to inclusions in basic irons for the Bast Furnace Committee of the Iron and Steel Industrial Research Council. Application of the process to the production of ingot moulds for steel ingot has also been made on a works scale at three steel works, the results of which are now under examination. The question of graphite refinement has been found to influence, directly or indirectly, the work and interests of practically every sub-committee in the Association, and during the year a meeting of chairmen resolved itself into a Graphite Panel, which has held three meetings to ensure fullest discussion and applications of the process. Practical works application of the process to crucible melted irons and irons from certain other furnaces is being made.

Work on the shrinkage and contraction of cast iron has been pursued actively throughout the year, and its first stage is now practically completed. Work on aluminium cast irons begun last year has been continued, and it is now practicable to produce sound cast irons, containing aluminium, of good mechanical properties and showing such resistance to heat at elevated temperatures as to justify extended trials where resistance to heat is required. The successful manufacture of sound castings now makes it possible to determine the properties of a range of aluminium irons. The aluminium cast irons appear to have unusually high strength at elevated temperatures.

Investigation of High Duty Irons

During the year under review the Association undertook, at the request of the Institution of Mechanical Engineers, an important investigation on high duty irons, planned in the first place to cover two years. This work follows logically from the Association's earlier work on inoculated irons, on irons containing additions of nickel, molybdenum and copper, and on the preliminary work carried out on heat treatment, followed by the work carried out at the National Physical Laboratory on combined stress and on crankshaft irons and steels. It is proposed to examine a complete range of irons of 1.5 per cent. carbon upwards, both plain and alloyed, and heat treated where this is necessary to secure the best properties. It is intended to establish the whole of the mechanical properties and data required for the use of such irons in engineering applications, and arrangements have been made for special mechanical tests to be carried out by Dr. H. J. Gough at the National Physical Laboratory.

The work of the Melting Practice and Sands Refractories Sub-Committees continued from last year in conjunction with the L.M.S. Railway Co. on the foundry and laboratory characteristics of a series of cupola cokes has been completed, and the results were embodied in a report by Dr. H. O'Neill, of the L.M.S. Railway Co., and the director of the B.C.I.R.A. to the June conference of the Institute of British Foundrymen at Derby. Some preliminary work has been done on the influence of tuyere size, blast pressure and volume on cupola melting efficiency.

The development of the balanced blast cupola has been continued. The total number of installations made or under construction is now 175, with an aggregate hourly capacity in excess of 1,200 tons. Fifty installations have now been made or are being made overseas. The average size installed has a capacity of seven tons per hour, but they range from furnaces of 21 in. diameter, yielding 1.8 tons per hour, to 66 in. diameter, yielding 17.8 tons per hour. A furnace of 81 in. bore is under construction in U.S.A., with a rated capacity of 26.8 tons per hour, and furnaces up to 90 in. bore can be designed. The fuel saving effected by these installations, apart from other advantages, may be conservatively estimated at £25,000 per annum. Although the statistical data available do not permit a reasonably accurate estimate, there is ground for believing that one-fifth to one-fourth of the cast iron now made in Great Britain is melted in the balance blast type of cupola, and includes both light and heavy castings, malleable cast iron, refined pig iron, and the melting metal for steel castings in the converter.

During the year under review Mr. W. Y. Buchanan addressed the Melting Practice Sub-Committee on the melting of borings and turnings in the cupola and the possibilities of extending the application of his proposals are being explored. The Rotary Furnace Panel of this sub-committee continues active.

Moulding Sands and Refractory Linings

An important investigation on the use of naturally occurring clays as bonds for mouding sands, both natural and synthetic, has been completed and reported to members. The examination of refractory linings of cupola and rotary furnaces in relation to service life has been continued, and work is also being carried out reviewing methods of testing moulding sands. The work begun by the Association over ten years ago on sand testing and control has been amply justified in view of the necessity for the close control of moulding sand in the mechanised and continuous production plants now being so widely adopted in the industry.

The Tests and Specifications Sub-Committee has been concerned with various methods for improvements in accuracy and speed of analytical methods. The Association has also actively co-operated with the British Standards Institution in the revision of British Standard Specification 321 (1928) for grey iron castings and the formulation of a new specification for high duty irons.

Following the revision of recommended analytical tolerances for foundry pig irons, the Pig Iron Sub-Committee has been engaged on a scheme for the grading of pig iron, now approaching completion. In this work the committee has had the active co-operation of members nominated by the various manufacturers' associations in the blast furnace industry. The White and Chilled and Malleable Cast Iron Sub-Committees have also been active, and reports of their deliberations have been made available to members.

Following two meetings of members interested in the vitreous enamelling of cast iron, two Enamelling Panels were formed, one for Scottish and the other for English members, and discussions have taken place of the lines on which investigation could be most profitably pursued. The work on graphite refinement and on clay-bonded synthetic sands is of

special interest to those engaged in vitreous enamelling and a number of practical problems have also been dealt with. Further informal discussions have taken place with representatives of the Institute of Vitreous Enamellers, who are also keenly interested in this subject, and it is hoped that co-operation will be established. It is therefore proposed to provide a full-time investigator for vitreous enamelling and to provide proper laboratory resources for tests on vitreous enamelled ware and materials used for manufacture.

During the year the development department of the Association, which assists members in dealing with practical and technical matters and advises on prospective developments, dealt with 1,217 inquiries, an increase of 27 over the previous year. The chemical laboratory carried out over 5,000 duplicate estimations and the metallographic laboratory made nearly 1,000 micro-examinations. In the mechanical testing laboratory 2,300 mechanical tests of various kinds were made; in the sands laboratory 1,900 tests on sands and refractories were made for strength, permeability and mechanical analysis; and in the melting shop 290 melts, crucible and cupola, were carried out.

On two occasions during the year the Association co-operated in a joint exhibit of the work of the country's research institutions, organised by the Department of Scientific and Industrial Research. The first occasion was the exhibition held at the Building Centre in London in March, 1937, and the second that of the Engineering and Marine Exhibition in London in September, 1937.

The accounts circulated to members with the 16th annual report show a total income for the year of £16,405, and a credit balance on the year's working of £1,494. The subscriptions qualifying for grant enabled a grant of £5,750 to be earned, out of a possible grant under the present arrangement of £8,500.

Removal of Electrodeposits of Nickel from Steel

Chemical Treatment as Alternative to Machining

NICKEL coatings can be completely removed from steel articles without appreciable attack on the steel by anodic treatment in 50 per cent. (by volume) sulphuric acid solution with an applied potential not exceeding 2.0 volt, according to a paper which Mr. G. E. Gardam read before the Electrodepositors' Technical Society at the Northampton Polytechnic Institute, London. The method is suitable for the removal of thick nickel coatings as an alternative to machining, which is expensive and removes some steel. It can also be used to determine the average thickness of nickel or of composite nickel-copper coatings on steel by loss in weight.

The Treatment Applied

The method consists essentially in subjecting the nickel coated article to anodic action at air temperature in a mixture (sp. gr. 1.545) of equal volumes of concentrated sulphuric acid and water, the potential difference between the anode and cathode being controlled so that it does not exceed 2.0 volts. The solution may be conveniently contained in a lead-lined tank, the lining being used as cathode; alternatively separate cathodes of lead or nickel may be used.

Control of the applied voltage may be attained by connection to a generator whose open circuit voltage is 20 volts or to a single lead accumulator cell. Where the available supply is at a higher voltage, the applied potential can be adjusted by manual control of a series resistance. Since the current falls and finally ceases when the nickel is completely removed, satisfactory control is more easily achieved if a further resistance is connected in parallel with the stripping bath. Alternatively a resistance carrying a sufficiently large current may be connected across the available supply and the stripping bath supplied from two tappings, the open circuit voltage between which is 2.0 volts. Articles placed in the bath connected in this manner may be left for long periods and removed when convenient, but the time of stripping is longer and the consumption of current is higher than by either of the previous methods.

The completion of removal of nickel is indicated by cessation of current in the stripping bath; agitation of the solution or removal and inspection of the article is undesirable as the unavoidable disturbance of the protective film results in further attack on the steel. The current density on the nickel surface is limited by the applied voltage to a low value and the time of stripping is in general greater than the time of depositing.

The concentration of sulphuric acid used is not critical; however, in more concentrated solutions, *e.g.*, 60 per cent. by volume, anodic dissolution of nickel at low voltage is extremely slow, apparently owing to the formation of viscous or gelatinous nickel compounds on the surface, which do not readily disperse in the solution. In less concentrated solutions, *e.g.*, 40 per cent. by volume, attack on the exposed steel is increased. The addition of 200 g. per litre of nickel sulphate ($NiSO_4.7H_2O$) to 50 per cent. (by volume) sulphuric acid solution appeared to be without influence on its use for stripping nickel; it therefore appears possible to operate the solution at least until the nickel content reaches a high value.

Before insertion into the bath, articles should be degreased and dried. Methods of degreasing as used prior to electroplating may be employed, but wiping with a cloth soaked in organic solvent followed by rubbing with a paste of magnesium oxide or precipitated chalk is also satisfactory. The process has been found to operate satisfactorily on articles of complex shape, *e.g.*, a nickel-plated sheet bent into the form of a long relatively narrow tube.

The selective action of the process appears to be due to formation on the steel surface of a protective film, possibly of sulphate. If this is not disturbed by agitation of the solution or by oxygen evolution, further dissolution of steel is prevented. The overall voltage at which oxygen evolution commences depends on a number of factors, *e.g.*, cathodic and anodic overvoltages and resistance of the solution: it may vary with conditions, but in experiments using a steel anode and a lead cathode in 50 per cent. (by volume) sulphuric acid solution, the minimum voltage at which visible oxygen evolution occurred on the anode was 2.4-2.5 volts. When the voltage exceeded this figure, attack on the steel was progressive and frequently localised. In the practical application of the process, it is desirable to limit the applied voltage to a maximum of 2.0 volts; at this voltage a satisfactory rate of removal of nickel is obtained without danger of oxygen evolution.

Nature of Attack on the Steel

The attack on the steel under the recommended conditions appears to be confined to that necessary to form a protective film and is not progressive. Thus in a number of experiments on mild steel in which the time of anodic action was varied, but disturbance of the protective film was avoided, the loss in weight was approximately constant at 0.01 g. per sq. in. independent of the time. The attack appeared uniform; a polished surface was rendered matt.

Immersion of steel or nickel-plated steel articles in the stripping solution without current does not result in severe corrosion. Thus a piece of mild steel and a similar piece coated with nickel over half its area were immersed in 50 per cent. (by volume) sulphuric acid at air temperature for 7 days.

The loss of weight was 0.023 g. per sq. in. in each case (calculated on the exposed steel only), equivalent to a loss of approximately 0.00002 in. thickness.

The recommended method may be used to determine the weight of relatively thin nickel deposits on steel applied for decorative and protective purposes. The nickel-plated area is estimated; the article is then degreased, weighed and made the anode in the sulphuric acid solution, supported by an iron wire or strip. Current is supplied from a single-cell lead accumulator or a potentiometer. To minimise attack on the steel, it is preferable to use a 55 per cent. instead of a 50 per cent. (by volume) solution of sulphuric acid. Care is taken to avoid disturbing the protective film and anodic action is continued for some time (*e.g.*, 15 minutes) after current has ceased to pass through the solution. The article is then quickly withdrawn, thoroughly rinsed, dried and reweighed. The loss in weight is that of the nickel coating together with some steel.

Error Due to Attack of the Steel

In this new analytical technique, the attack on the steel can be reduced by careful operation to about 0.005 g. per sq. inch, equivalent to an error of + 0.00004 in. The error may be partially eliminated in the following manner, depending on the fact that attack on steel is confined to the formation of a protective film: After reweighing, the steel article is replaced and again subjected to anodic action under the same conditions for a short period, *e.g.*, half an hour, washed, dried and reweighed. The loss in weight is deducted from the previously obtained figure, the difference being the weight of nickel coating alone. Taking the density of nickel at 8.9, the weight of a coating 0.001 in. thick is 0.146 g. per sq. in. (0.01 mm. thick = 0.0089 g. per sq. cm.).

Electrodeposits on steel, externally of nickel, are sometimes composite and consist of layers of nickel, copper and nickel or of copper and nickel; the copper deposit is sometimes polished before the application of the final nickel coating. Anodic solution of copper by the method described above tends to be arrested after solution of some copper has occurred, but the amount of the attack, together with the possibility that the copper layer is not continuous or is very thin locally, renders the method in general unsatisfactory for estimation of the individual layers of a nickel-copper-nickel coating.

Total Weight of Composite Coating

By slight modification, the method may be used to determine the total weight of the coating and, in view of the small difference in density of copper and nickel, the inaccuracy in the calculated thickness is small. The procedure described above is followed as far as the first reweighing; if copper is apparent the article is made anode at a current density of 5-15 amps. per sq. ft. in a solution of ammonium sulphate 50 g., ammonium hydroxide (sp. gr. 880) 50 ml. per litre, until copper is removed. The surface of the solution is preferably covered with a layer of oil to prevent loss of ammonia. The article is removed, rinsed and dried, and if nickel is still present it is replaced dry in the sulphuric acid solution and treated as described for a nickel-plated article.

Surface State and Corrosion

Research Carried Out at Cambridge

DR. U. R. EVANS, in a paper read before the Chemistry Section of the International Congress of Physics, Chemistry and Biology, at Paris, September 28 to October 9, gave preliminary notes based on the principles of research carried out at Cambridge on surface state and corrosion. He said that the direct union of metals with oxygen produces a visible scale at elevated temperatures, interference colours at intermediate temperatures, and, at ordinary temperatures, a film which is invisible in pure dry air. To study this invisible oxidation it is useful to employ an electrical or optical method; the thickness of the invisible film which is formed on an unpolished surface is greater than on a polished surface. Copper, exposed to air containing hydrogen sulphide at ordinary temperatures, develops the same sequence of interference colours which in pure air are only produced at elevated temperatures; the preliminary exposure to pure air diminishes this tendency to tarnish in contaminated air.

Conditions of Formation of Surface Films

The film of chrome iron remains protective in the presence of damp air, but the film of ordinary iron always has feeble points where corrosion can commence when drops of water remain on the surface. The "conditional velocity" increases, but the "probability" of attack diminishes, with an increase in the concentration of oxygen, because at a high concentration of oxygen the transformation of ferrous hydroxide into hydrated ferric oxide can occur in physical contact with the surface—so that the attack chokes itself. As a result of this tendency to choke itself, direct attack is often without importance at ordinary temperatures. On the other hand, electro-chemical attack is often very important, because such an attack does not choke itself, if the cathodic and anodic products are quite soluble; for example, iron in sodium chloride produces iron chloride and sodium hydroxide and the production of rust occurs beyond the physical contact of the points of attack. Research at Cambridge shows that the electric currents which pass on the surface of iron, are, in general, big enough to explain the corrosion observed.

In the liquids intermediate between the class which produces corrosion and the class which produces passivity, a new line can constitute the place of the origin of corrosion; in this case preliminary exposure to air (to repair the oxide film along the line) diminishes the probability of attack, which is shown by statistical research with sodium bicarbonate. An austenitic steel (with 18/8 chrome nickel) which ordinarily resists sea water, undergoes local attack at a place where the surface has been recently cut; there are a number of cases where a metal which is sufficiently resistant to the ordinary atmosphere, if a polished surface is exposed, undergoes a local attack if lines or scores have been engraved on the surface. Certain inclusions (notably sulphides) can constitute the points of corrosion on a polished surface (but not on an unpolished surface, where the cuts are more susceptible points than the inclusions); the inclusions of silicate are not without danger. The unfavourable influence of sulphur on the resistance of iron to citric acid can be corrected by the presence of copper, because copper sulphide is not dissolved by feeble acids.

Mechanical Properties of Tin Bronzes

THE proportion of tin used in bronzes intended for cold-working may amount to seven or eight per cent. usually but recent work suggests that there are advantages attaching to the use of as much as 14 per cent. of tin. Dr. H. Lepp, of the Compagnie Générale d'Electro-Metallurgie, Paris, has found greatly improved elongation and malleability in bronzes of this kind which have been properly degassed. His results are summarised in Technical Publication, Series D, No. 3, issued by the International Tin Research and Development Council, from whom copies may be obtained free of charge.

Some Recent Metallurgical Patents

Magnetic Alloys

IN the manufacture of magnetic materials having a high initial permeability and composed of alloys having as the main constituents 35-50 per cent. of nickel, 65-40 per cent. of iron and with or without up to 16 per cent. of other metals such as manganese, titanium, copper, or aluminium, the material is cold worked to produce an elongation considerably exceeding 100 per cent., is then annealed at 900-1,200° C., and is finally cold worked to produce an elongation less than the first elongation. The cold working may be effected by rolling, and the annealing time may be less than 1 minute or not more than 30 minutes, the temperature and time given in an example being 1,100° C. and 10 minutes. The annealing may be effected in an annealing furnace whereby the material is cooled rapidly. See Specification 463,901 of Heræus Vacuumschmelze Akt.-Ges.

Copper Alloys

COPPER alloy castings are produced by adding 0.2—2.0 per cent. of chromium to the copper with or without suitable deoxidants, casting the alloy and then heating the casting to 300—700° C. The deoxidants employed are zinc sodium alloy, cadmium sodium alloy or one or more of the substances calcium, silicon, beryllium, calcium boride or boron carbide and the metal may be covered with charcoal or a flux such as borax or glass during melting and casting. The chromium may be added to the copper in the form of a master chromium-copper alloy containing 10 per cent. of chromium and one or more of the metals, lead, silver, zinc and cadmium in a total amount not exceeding 5 per cent. may be added to the alloy before casting. In an example, an alloy contains in addition to the chromium content above 1 per cent. of cadmium, 1 of zinc, 0.5 of lead and 0.10 of silver. See Specification 461,845 of Neave, D. P. C. and Miller, H. J.

Titanium Steel

IN the production of titanium steel, an iron bath is covered with a slag which is as free as possible from silicic acid and contains titanic acid and lime in the proportions of 70 to 30, and from this slag, by reduction with carbon, titanium is introduced into the iron bath in a quantity which is sufficient to remove the nitrogen, sulphur, and oxygen contained in the bath into the slag in the form of titanium compounds and then to convert all the carbon of the iron bath into titanium carbide corresponding to the formula TiC, the amount of titanium in the steel not exceeding 3 per cent. If a phosphorus-containing iron bath is used, the process is carried out to yield a steel containing 0.05—0.5 per cent. of phosphorus and a titanium carbide content of 0.5—1.0 per cent., such a steel being suitable for structural purposes. If the steel is required to be corrosion-resistant, the proportion of phosphorus exceeds 0.5 per cent. but does not exceed 1 per cent. Titanium steels for deep drawing sheet are produced by adding to the steel containing not more than 0.5 per cent. of titanium carbide, 0.3 per cent. of silicon and 0.1 per cent. of aluminium, and for transformer stampings 4 per cent. of silicon and 0.1—0.5 per cent. of aluminium. See Specification 459,432 of Mathesius, W.

Mixed Metallic Carbides

MIXED carbides containing boron carbide are obtained by subjecting a mixture of carbon and boric acid to fusion by electrothermic heating, comminuting the resulting mass, mixing a further quantity of boric acid with it and then heating the mixture to fusion electrothermically, a metal capable of forming a carbide, or a compound of such a metal, or a mixture of such compounds or metals being added to the parent materials or to the intermediate product. Suitable metals include aluminum, titanium and manganese. The process may be conducted under raised pressure and with the addition of substances which promote fusion and the formation of carbide. See Specification 464,182, of Wacker Ges. für Elektrochemische Industrie Ges.

Corrosion-Resistant Alloys

A corrosion-resistant alloy comprises 25-80 per cent. of iron, 5-25 per cent. of phosphorus, 4-70 per cent. of copper, and 0-30 per cent. of one or more of the metals antimony, arsenic, bismuth, cadmium, chromium, manganese, molybdenum, tin, tungsten, vanadium, zinc. Aluminium is excluded from the alloy and silicon does not exceed 0.5 per cent. Specific examples are given of alloys of iron, copper, phosphorus, tin; iron, copper, phosphorus with silicon, manganese, carbon as impurities. Scrap metal may be used in making the alloy; for instance, brass scrap may be used to introduce copper and zinc together with small quantities of antimony, arsenic, bismuth, cadmium, and tin. Calcium phosphate may be used to introduce phosphorus and as a flux. See Specification 464,095 of R. B. McCauley.

Annealing Magnesium Alloys

MAGNESIUM alloys contain aluminium and silver, with or without one or more of the metals manganese, zinc, and calcium. They may contain up to 11 per cent. of aluminium and silver together, 6-8 per cent. of aluminium, and 1.5-3 per cent. of silver, with or without up to 4 per cent. of manganese, and up to 6 per cent. of zinc or calcium. The alloys may be heated to about 400° C. for 15 minutes or more, and then hardened by heating to 130-220° C. for one or more days. Specification 464,030 of J. L. Haughton and W. E. Prytherch.

Refining Lead

LEAD containing small quantities of bismuth and one or more alkaline earth metals is refined by incorporating therein antimony or arsenic or both, the dross formed containing the bismuth and alkaline earth metals being thereupon separated. The process may be applied to lead which has been previously debismuthised with alkaline earth metals, *e.g.*, calcium and magnesium, to effect a further lowering of the bismuth content. The antimony and/or arsenic may be added in metallic or alloy form, *e.g.*, as lead-antimony and/or lead-arsenic alloys. Lead-antimony and lead-arsenic alloys containing 90.53 per cent. of antimony and 6.2 per cent. of arsenic respectively, are referred to. See Specification 464,252, of American Smelting and Refining Co.

Distilling Magnesium

MAGNESIUM is produced by reducing calcined magnesite alone or calcined dolomite alone with silicon, ferro-silicon or like material containing available silicon, four or more molecules of base beng present to each molecule of silicon. See Specification 464,438, of I. G. Farbenindustrie.

Heat Treating Light Metals

LIGHT metals and alloys, particularly aluminium and its alloys are heat-treated in molten baths which contain as their main constituent alkali halides or a mixture of a plurality of alkali halides and basic-reacting substances in such quantities, not exceeding 30 per cent., that the metals, etc., are protected from attack by the halides. The bath may also contain one or more alkaline earth halides. As basic-reacting compounds the oxides, carbonates or hydroxides of alkaine or alkaline earth metals, basic-reacting phosphates, tungstates or borates as well as oxides such as aluminium or magnesium oxide may be used, or compounds such as aluminium or magnesium oxide may be produced in the bath from the corresponding light metal or alloy, the formation of the basic-reacting compounds being promoted by temporarily raising the bath temperature, blowing oxygen, *e.g.*, as air through the bath or adding peroxides such as calcium peroxide. The temperatures used are 300-350° C. In an example aluminium is treated in a bath having a temperature of 530° C. and containing 48 parts of calcium chloride, 31 parts of barium chloride and 21 parts of sodium chloride to which is added 10 per cent. of barium carbonate. See Specification 464,697, of Deutsche Gold-und Silber-Scheideanstalt Vorm. Roessler.

Metallurgical Section

December 4, 1937

The Testing of Coke

A RECENT Bureau Report (No. 169) of the British Cast Iron Research Association relates to the testing of coke. According to Mr. C. Rowley certain qualities of coke confer on it a special value, and although some of these can be assessed by laboratory tests, the results do not always agree with the behaviour of the coke when in the blast-furnace or the cupola.

In this country, research has been carried out systematically on the properties of coke since 1926, when the Midland and Northern Coke Research Committees were formed with headquarters at Sheffield and Newcastle respectively, the Scottish Coke Research Committee being formed during 1928 with headquarters in Glasgow. The main object of these coke research committees has been to devise methods of testing which express the value of the coke for industrial purposes and to investigate the factors which determine the quality, as well as to devise methods for improving the quality of the coke. The work of the various committees on metallurgical coke has been carried out mainly from a blast-furnace point of view, but tests have been made on cupola coke, particularly by the Northern Committee.

The properties required in a satisfactory metallurgical coke are somewhat similar, whether for blast-furnace or cupola use, and therefore the chemical and physical tests used by the coke research committees should be of interest to founders. Their conclusions respecting quality and methods of manufacture are, of course, of primary interest to coke makers, but the methods of testing are also of great interest to users for the purpose of controlling supplies, and these tests and conclusions are ably reviewed in Mr. Rowley's report. Size analysis, shatter test (to indicate the liability of the coke to form breeze when it is dropped), critical air blast, wet oxidation tests (giving the rate of evolution of carbon dioxide from a graded sample of coke in a mixture of chromic and phosphoric acids at a temperature of 100° C., and which indicates the relative amounts of graphite present in any series of cokes), apparent density, apparent porosity, combustibility and reactivity (which is a measurement of the degree of reaction of the coke with an oxidising agent such as carbon dioxide or steam) are each dealt with in turn.

Current Cast Iron Research

THE present research and development programme of the British Cast Iron Research Association includes further work on the formulation of graphite. A study is being made of the effect of cupola operation on the formation of graphite, with respect to blast volume and pressure, height of bed, nature of coke and nature of charge, and of the production of graphite-refined and inoculated irons from the point of view of their respective non-metallic inclusions and their modification by ladle additions.

In co-operation with the Oxygen Panel of the Iron and Steel Institute, the alcoholic iodine, chlorine and electrolytic methods for the estimation of inclusions in pig and cast irons, are under investigation. An attempt is being made to apply the graphite-refining process to crucible-melted cast irons. The shrinkage and contraction of cast iron is also receiving additional attention, mainly in a study of the influence of phosphorus content, mould conductivity and permeability, and cupola conditions, and it is hoped to obtain quantitative data on liquid and solid shrinkage, freezing points and fluidity of various compositions, and also to measure temperature gradients in the mould. With regard to high duty irons, the Association is investigating the founding and mechanical properties and structure of cast irons, both plain and alloyed with nickel, molybdenum, copper and chromium within the range 1.5 to 3.5 per cent. carbon, heat-treated where necessary. This investigation is sponsored by the Institution of Mechanical Engineers and is being supported by other interested bodies.

The origin of defects in enamelled ware in relation to the presence and size of iron carbide, graphite and slag, and other non-metallic inclusions is also under investigation, such defects being considered in relation to the moulding sands used and to methods of shot blasting. In this it is hoped to assist members in overcoming difficulties due to the occurrence of enamelling defects and in establishing criteria by which the quality of enamelled finishes may be judged. A study of cupola design with reference to tuyere size, blast pressure and volume and their influence on melting efficiency is in progress in that part of the programme which relates to melting practice.

Magnesium Alloys at High Temperatures

A NUMBER of the possible future uses of magnesium alloys involve the exposure of the metal to elevated temperatures, and for this reason the investigation of the mechanical properties of such alloys when hot has become important. Such investigations have been carried out at the National Physical Laboratory with the object of finding alloys which would probably behave satisfactorily when exposed to stresses at elevated temperatures.

Silver increases the ultimate strength of magnesium up to 290° C., but its effect when used alone is not so markd as that of aluminium. Cerium, based on a study of cerium-magnesium and cerium-calcium-magnesium alloys, has been found to have a pronounced effect in increasing the strength at elevated temperatures, and even small quantities of the order of 1.0 per cent. have a remarkable effect in increasing the hardness at 300° C. The addition of a small amount of calcium to the cerium-magnesium alloys appears to be beneficial in preventing oxidation during melting and heat treatment, and also in improving the

age hardening properties. The increased hardness due to heat treatment, however, is relatively small even when calcium is present. A harder alloy can be produced by adding nickel to the cerium-magnesium alloys, but such nickel alloys are very liable to corrosion; replacing nickel with cobalt and manganese slightly reduces the extent of any such corrosion. Some valuable information upon this aspect of the use of magnesium and its alloys in industry was published by the Department of Scientific and Industrial Research in September of this year, in the form of a special monograph under the title of " Magnesium and its Alloys."

Magnesium alloys at present used in industry are almost entirely confined to alloys with aluminium and zinc, often containing a small amount of manganese introduced to improve corrosion-resisting properties. With alloys containing 8 per cent. or more of aluminium, it is usually possible to produce increased hardness and a general improvement in properties by suitable heat treatment. This takes the form of exposure to a temperature of 420° C. for a few hours, sometimes followed by tempering for four to seven days at about 150° C. Increased ductility can be produced by adding cadmium to magnesium.

Electrolytic Production of Manganese

MANGANESE is one of the metals which has not yielded readily to electro-deposition in the pure state. For that reason work carried out by Koster and Shelton at the United States Bureau of Mines (*Engineering and Mining Journal*, vol. 137, No. 10) marks a definite step in the solution of the problem on a commercial scale. These investigators found that electrolytes containing manganese sulphate gave non-metallic deposits on the cathode, and that in the presence of ammonium sulphate or chlorate metallic deposits could be obtained only with current densities above 100 amperes per square foot; in other cases fouling took place in solution and the cathodes merely turned black in the presence of manganese. Some progress was ultimately made by placing a diaphragm between the cathode and the anode and by adding an excess of manganese carbonate to the electrolyte, which was composed of manganese and ammonium sulphates. Under these circumstances, when the anolyte was agitated the manganese carbonate in suspension neutralised the acidity caused by the sulphuric acid which was formed. Manganese of a purity of 85 to 95 per cent. could then be deposited continuously for periods of 72 hours or more, but the resulting deposits were rough and the formation of " trees " eventually caused a gradual drop in the rate of deposition to zero.

By arranging conditions so that the sulphite ion was present in the catholyte in a concentration of the order of 0.1 gram per litre, it was found that deposits of a purity of 99.6 to 99.8 per cent. could be obtained. The sulphite ions were added as ammonium sulphite, as sulphurous acid, or in the form of sulphur dioxide gas. The development of this idea in conjunction with suitable circulating systems then indicated that manganese could be definitely regarded as a metal which might be recovered by electrolytic deposition on a commercial scale. A semi-commercial plant is now in operation at Reno, Nevada, where the process will be developed by the United States Department of Mines for ultimate control by licence in the United States. Parallel with these developments experimental work has been done in Canada by Shelton, working at Montreal, and the process is now being developed in Canada for licence in all countries other than the United States.

World Consumption of Non-ferrous Metals

THE necessity to meet a materially increased demand for non-ferrous metals during 1937 has led not only to the re-starting of plant which had hitherto lain idle, but has also brought about the extensions of many works and the erection of new plant, especially on the Continent, both in mining and the dressing of ore and in the metal smelting and refining industry. A few years ago in the period of depression an endeavour was made to balance production in relation to reduced consumption by decreasing the production and thereby equalising the markets, but at the present day the position is just the opposite, and an endeavour is being made to satisfy increased demand by the extension of production in order to prevent any market disturbances or unsound rises in price.

In order to bring about this state of affairs, the existing international metal cartels and similar organisations have allowed their members far-reaching liberty as to the extent of their production. For instance, copper production by producers adhering to the agreement of the large copper producers, operative until July, 1938, was made free as from January, 1937; the export quotas of producer-members of the tin cartel were increased in 1936. According to statistics which have been compiled and studied by the Metallgesellschaft A.G., of Frankfort-on-Maine, however, about 56 per cent. of the total world consumption of copper, lead and zinc during 1936 had to be covered by imported raw materials, either in the form of finished metal or in the form of smelting and refining materials, and only about 44 per cent. of the total consumption could be covered by home mining production at the time and by home supplies of scrap material. The metal content of European mining production expressed as a percentage of European metal consumption during 1936 was 52 per cent. for zinc, 30 per cent. for lead, 20 per cent. for copper, and only 4 per cent. in the case of tin.

An Italian " Three-Year-Plan "

WHAT amounts to a " three-year-plan " for iron and steel production in Italy was announced at a recent meeting of the Corporation for the Metallurgical and Mechanical Industries, at Rome, when it was decided that 3,000,000 tons of iron and steel must be produced entirely from Italian resources by 1940. The principal obstacle in the way of carrying out this plan, however, appears to be that of finding the fuel necessary for smelting, because Italy produces very little coal. This obstacle may eventually be overcome by increasing the use of electric furnaces, the current for which may be obtained from hydro-electric plant. Electric furnaces have already furnished only 25 per cent of the steel produced in Italy, so that the electric furnace capacity will have to be increased materially to achieve desired production without using imported coal. Italy is expected to find about 500,000 tons of scrap iron and steel by 1940, and it is interesting to note that imports of scrap declined from 915,000 tons in 1935 to 365,000 tons in 1936, but increased again to 279,000 tons during the first half of the present year.

Memories of Electroplating and Electroplaters*

By
W. R. BARCLAY, O.B.E.

LOOKING back, I find it difficult to estimate the relative value, to me as an industrial metallurgist, of my experiences in casting and rolling on the one side and those in electroplating on the other. Of one thing I am sure, and that is that both were of value, and I would urge that the younger men coming into the plating industry should have some knowledge of general metallurgy. I would particularly emphasise the importance of a study of the physical condition of metallic surfaces used for electroplating and its influence on the quality of the electrodeposit, its adhesion and structure; more especially the bearing of these factors on the final processes of polishing.

It was in the late nineties that I was first called upon to design and lay down an electroplating plant. The literature available at the time was very limited. Our main sources of information in the English language, apart from the very interesting but out-of-date work by Smee (1841), were Dr. Gore's well-known "Art of Electro-Metallurgy," first published in 1877; the same author's text book on Electro-Chemistry, 1885, and his "Art of Electrolytic Separation of Metals," 1890. A number of scattered articles in various popular and semi-popular technical journals appeared from time to time in the last decade of the century, as did also some handbooks on specific subjects, such as Urquhart's "Electrotyping and Electroplating," but for the most part these dealt with laboratory investigations and experimental work and afforded little assistance to the industrial worker. Probably the works of most practical value at this particular period were McMillan's "Treatise on Electro-Metallurgy—the first edition of which appeared in 1890, revised and almost rewritten in 1899, and the well-known Treatise by Langbein, translated from the German.

Electro-Silver Plating

I had, amongst other things, to put down a series of vats for electro-silver plating, and, of course, make up the electrolyte. The standard method usually adopted for new silver plating solutions at that time was to take a small quantity of old solution from an existing bath, add a large quantity of potassium cyanide solution and supply the necessary silver content by what is known as the "battery process." For various reasons I adopted a chemical method of making up the bath, and in doing so departed from convention in that, instead of following the laborious processes of dissolving metallic silver in nitric acid and afterwards precipitating with potassium cyanide or chloride, I purchased silver nitrate direct from some of the larger silver refiners, but I was very severely criticised and informed by several "practical" platers that my solution would never work, and that nitrates were fatal impurities. It was in vain that I tried to explain the simple chemistry of the process and that the resulting potassium nitrate was washed away in the filtrate, my critics were quite satisfied that I was far too much a theorist to make an electroplater.

My critics of those days were for the most part very good-natured, and I owe much to the stimulus of their comments. More than once, indeed, their practical experience placed freely at my disposal was invaluable, and I came to have the greatest respect for those nineteenth century electroplaters. Although possessing scarcely a shred of knowledge of chemistry, they were able to carry out such chemical operations as, *e.g.*, the manufacture of potassium cyanide from prussiate of potash and carbonate with, considering the crudeness of their equipment and the quality of their raw material, truly amazing skill and judgment.

Considerable practical experience had been gained in silver plating over more than a generation prior to the time of which I speak, and it must be said that the standards reached were surprisingly high in view of the limitations of theoretical knowledge. The main difficulty continuously encountered was the familiar one of imperfect adhesion, and fairly considerable variation in the structures of deposits. There were, however, many other technical questions to which no really adequate answers were forthcoming, *e.g.*, the relationship of the factors of metal ion concentration, free cyanide, current density, and particularly the influence of both organic and inorganic impurities in the electrolyte. Our imperfect knowledge on these points resulted in many minor troubles which are now almost unknown.

Amongst the minor difficulties was that of the varying hardness of silver deposits, which often led to polishing troubles and unsatisfactory surface finishes. Most of these were found on investigation to be due either to excessive content of free cyanide or to too low metal concentration. The latter was particularly common among platers who were anxious to economise in the amount of silver in stock. I had occasion over a term of years to examine many such solutions, and found that some of them contained as little as 5-7 dwts. of silver per gallon.

Electrodeposition of Gold

With regard to the electrodeposition of gold I would like particularly to mention the name of Millward, the discoverer of the influence of carbon bi-sulphide as a brightening agent in silver plating. Millward had established an electroplating plant in Sheffield, and he and his staff there built up a high reputation for electro-gilding, although they surrounded their methods with strict secrecy. One particular difficulty of the art was the gilding of brightly-burnished surfaces. The cyanide solutions were, of course, in general use, and worked at temperatures varying from 45 to 60° C. Within this temperature range the reactions of free potassium cyanide on bright silver surfaces were very delicate, and it was essential to connect up the current simultaneously with the insertion of the metallic surface to be gilded, otherwise the degree of polish was appreciably reduced with the effect of "clouding" of the gold deposit. I, personally, found it advisable to recommend a reduction of the amount of free cyanide present to a minimum, and to keep up the metallic concentration of the electrolyte by regular additions of good fulminate with just sufficient cyanide to effect complete solution.

In 1898, I carried out a series of experiments in the electrodeposition of platinum and gold in the form of partial or sectional deposition, in which alternative sections of the article being treated were "stopped off" and alternate deposits of each metal applied. For this purpose I found the solution of Roseleur's to be reasonably satisfactory. It is essentially a phosphate solution containing an excess of sodium phosphate. The greyish-toned colour of platinum from this electrolyte contrasted admirably with the rich yellow of the gilding bath, especially one containing not less than 3 oz. of gold per gallon. Applied to ornamental articles such as bowls, cups and trophies, the effects were really very beautiful.

Nickel Plating

The practice of nickel plating in this pre-War period was on a very limited scale indeed as compared with the post-War period, and experience was therefore correspondingly restricted. The electrolytes used were almost invariably the double sulphates of nickel and ammonium worked at normal temperatures and at a low current density. Deposits were for the most part very thin. The passivity of relatively pure nickel anodes, particularly in the rolled condition and the rapid formation of the well-known black surface sludge militated severely against the attainment of thick deposits. Most nickel platers demanded an impure anode in order to obtain

* Extracts from a lecture delivered before the Electrodepositors' Technical Society.

a product which would satisfy the nickel plater from this point of view.

It was rare to find anodes of more than 96 per cent. purity—usually, indeed, they assayed 90-93 per cent. Although Mond Nickel of 99 per cent purity was fairly well known and marketed as early as 1900, it was some years afterwards before it was adopted for the manufacture of anodes, and even then was the subject of many complaints. The backward state of the nickel plating industry at this period was undoubtedly due, amongst other factors, to the want of knowledge regarding nickel itself, and its properties. Even so scientific a worker and authority as Gore in his " Art of Electro-Metallurgy " (edition 1900) wrote " Nickel should not be employed for coating the interior of cooking utensils because of its being corroded by acids and having poisonous properties." I have already referred to the fact that the common electrolyte of those days was the double nickel ammonium sulphate salts, and such additions as were made had the general aim of improving the conductivity of the bath. Additions of boric acid were sometimes made and almost invariably the solutions were, of course, kept slightly acid. Few platers at that time had any knowledge of *p*H values, and chemical tests were confined to the occasional use of litmus paper.

I have not been able to obtain any exact figures of the scale on which electro-nickel plating was carried on at the end of the 19th and beginning of the present century, but from such records as I have access to I have estimated that the total consumption of nickel for the purpose in this country arely exceeded 80-90 tons per annum. It is only necessary to compare this figure with the current year in which the consumption of nickel anodes alone, apart from the nickel content in salts used for making up baths, will amount to well over 1,000 tons, in order to realise the progress made in this branch.

Electrodeposition of Copper

My experience of the electrodeposition of copper was confined mainly to its use as an intermediate coating in preparation for silver or nickel plating and therefore necessarily of the cyanide solutions. The most notable advance in practice in those days was the introduction of the combined cleaning and coppering solution for steel, made up, as you are aware, by increasing the proportion of free cyanide and adding a liberal quantity of sodium or potassium carbonate, working the solution at a fairly high temperature and current density. The process was, and is, very efficient, but it is distinctly advisable to spend a litte time and effort in a preliminary removal of the superficial dirt and grease adhering to the surface of the metal as it comes into the plating room. I have seen a number of cleaning and coppering baths ruined by continuously passing work through which was not only covered with grease, but particles of grinding and polishing powders, rouge, lime, tripoli compositions, etc.

There were wide differences in the methods adopted for making up the cyanide copper solutions. In my opinion, one of the most satisfactory for the workshop was to dissolve copper carbonate in potassium cyanide with the necessary addition of free cyanide. The carbonate salt can be readily obtained by precipitation from the sulphate solution and its direct solution in potassium cyanide gives automatically an addition of potassium carbonate, which undoubtedly increases the conductivity of the electrolyte. An alternative method of making up a cyanide copper bath which was also very popular, was to add ammonia to a solution of copper sulphate until the precipitate was entirely redissolved, giving the characteristic rich deep blue solution of cuproammonium sulphate, then adding sufficient potassium or sodium cyanide solution to discharge entirely the blue colour and obtain the clear colourless solution of the double cyanide. A small addition of potassium bisulphate was often made to improve the conductivity of the bath.

Work at the Sheffield Technical School

Much experimental work was done in the Sheffield Technical School during the period I have reviewed. In addition to such subjects as I have already referred to, *e.g.*, the influence of potassium carbonate and other so-called impurities in silver-plating baths, the substitution of sodium for potassium cyanide, some work was also carried out on the electrodeposition of the base metals, lead, tin, zinc and cadmium, and specimens coated with each of these were exhibited at various public and semi-public lectures and functions in Sheffield. I wish also to mention the researches of Professor Hicks and O'Shea on electrolytic iron in the earlier days of this period. Hicks was the principal of Firth College and a close friend of Sorby, the pioneer of the use of the microscope in metallurgical investigations. He later became vice-chancellor of the University of Sheffield. O'Shea was professor of applied chemistry. These workers carried out a beautiful series of experiments in the production of electrolytic iron which have by no means received the publicity they deserved. With a view to obtaining a product practically sulphur-free, the electrolyte chosen was a chloride in the form of double ferrous ammonium chloride, $FeCl_2 2NH_4Cl$. An absolutely necessary precaution taken was to ensure that any ferric compound present was reduced to the ferrous condition and when any fresh material was added to the electrolyte the solution was thoroughly shaken with reduced iron powder. The metallic concentration used was approximately 2 oz. per gal., and to maintain this, periodic additions of ferrous chloride and ammonium chloride were made. The resulting deposit was almost absolutely pure iron.

Chemical Colour Finishes for Metals

Standard Specifications Drafted by Electrodepositors' Technical Society

CHEMICAL colour finishes upon metals was the subject of a report of the Standards Committee presented at the annual meeting of the Electrodepositors' Technical Society, held at the Northampton Polytechnic Institute, Clerkenwell, London, on November 18.

Mr. E. A. Ollard, hon. secretary of the Standards Committee, said a draft specification for the nomenclature of the chemical colour finishes had been drawn up and was now ready to be submitted to the B.S.I. The object of this specification is to produce a standard method of defining the finish required, so that the purchaser may be able to obtain a reasonable uniformity in metal fittings ordered from different sources. It related to chemical colour finishes on copper, copper alloys and silver surfaces, and the finishes referred to are those in which the metal itself gives the necessary colouring, either by its intrinsic colour or by interaction with reagents.

The object of the specification is to enable the purchaser of metal articles finished by metal colouring to obtain the finishes he requires without the necessity of submitting a sample. Hitherto, considerable confusion has existed in the naming of the various finishes, and there is also no uniformity in this respect between different districts, also a title such as " oxy-silver " may cover a range of finishes according to whether the " relief " is bright or dull, and to what extent it is carried out. It has been decided to define the finishes with regard to three characteristics: (1) Nature of the surface, (2) colour, and (3) relief of the colour.

The nature of the surface is divided into four classes. " Polished " surface may be regarded as a metal surface after it has left the final polishing operation; it is also the starting

point for the three subsequent surfaces. " Satin " surface is a polished surface which is broken by pumice powder or a fine emery between the grades of ooo and o. This surface is intended to reproduce that of satin, which shows a different effect according to the way the light strikes it. The lines can be parallel throughout the whole article, or may follow some definite pattern, for example, round the edge of the article. " Egg shell " surface is slightly matted, such as would be produced by a light etch or scratch-brushing. The roughening effect in this case has no orientation, being in the form of dots or squares, and therefore looking the same whichever way the light falls upon it. " Frosted " surface is similar to egg shell, but the matted effect is deeper. Such a surface is obtained by sand or shot-blasting, or by chemical etch, or by depositing upon the surface a thin layer of copper from an acid copper solution without addition agents. It is, of course, understood that these four surfaces have for the most part no definite demarcation. It is felt, however, that if a surface is required lying between those defined, some idea can be given as to what is required from the above.

The colours covered by the specification are those produced by interaction of a metal surface with a chemical re-agent only, and do not owe their origin to lacquer or paint films. It is, however, admissible in certain cases to use transparent lacquers which slightly alter the nature of the colour. The colours under the heading of " natural metal surfaces," are the colours of the natural metal surface itself, such as silver, copper, brass and bronze. The colours of the alloys, however, may vary somewhat with their composition, and if an exact match is necessary this should be stated. " Sulphide finishes " (commonly known as oxydised finishes) are produced on metal by the action of sulphide solutions which form a coating of metal sulphide over the surface. The finishes under this heading are taken to be those in which the formation of a sulphide layer has been allowed to proceed to completion. " Steel finishes " are those produced by arsenical solutions. Under the heading " thin sulphide finishes " it is possible to obtain a range of colours according to the nature of the starting surface, and the thickness of the sulphide film produced. This film gives a colour, partly due to its own intrinsic colouring, and partly due to interference colours; also the underlying metal may itself show through to some extent. These colours are generally produced on copper or brass, although for some purposes the brass may first be treated with acid to leave the surface rich in copper. The four most usual finishes in the thin sulphide range are coinage, bronze, chocolate bronze, and B.M.A. It is hoped later to be able to give laboratory methods by which a standard sample of each of these finishes may be produced for comparison purposes.

The metal surface after colouring may have some of the colour removed by mopping, scratch-brushing or scouring. This process is called " relieving." In " no relief " the metal surface is left with an even coat of colour all over it. In " bright relief " the relief is done with a mop, so that the metal colour and the metal showing through have a polished appearance. " Dull relief " is done by scouring so that the metal colour and the metal surface showing through have a matt appearance. It is also necessary to define the extent to which the relieving is carried out. " Maximum relief " is understood where the relieved or metal surface predominates, the colour showing only to a small extent in recessed portions of the pattern (such finishes are known at the present moment as " antique"); in " minimum relief " the metal colour predominates and the metal shows through at a comparatively small number of places (these finishes are now known as " oxidised.") " High light relief " and "specified relief " are also defined.

It is suggested that metal finishes already known by trade names should be redefined under the above scheme, and also that this scheme should be submitted through the British Standards Institution to bodies representing the purchasers of such finishes, so that some uniformity in the ordering of these may be obtained.

Tin and Tinplate in Industry

Recent Publications of the International Tin Research and Development Council

A REVIEW of present knowledge on the wetting of metals by molten metals, with particular reference to tinning and soldering, by E. J. Daniels and D. J. Macnaughtan has been issued by the International Tin Research and Development Council as one of their technical publications (Series B., No. 6).

Wetting is a chemical phenomenon akin to adsorption, and although it has been closely studied in the case of liquids in contact with liquids, there is not much accurate information on the wetting of metal surfaces and on the surface forces involved. The attractive forces at the surface of solid metal must be large enough to overcome those within the molten tin or solder. Wetting occurs most readily when the metals concerned form compounds easily; for example, tin in quite small amounts enables lead or bismuth to wet copper. Fluxes are complex in their action. Further work may explain why, if fluxes lower the surface tension of the molten metal so that it can spread more readily on the solid metals, they do not hinder penetration into capillary spaces such as the joints in can bodies. There is a critical temperature above which each metal spreads rapidly and in some cases there is a period of induction before wetting occurs. Reference is made to the halo effect observed in the spreading of certain molten metals.

The effect of neutral solutions on tin is referred to in another technical publication. Tin, alloys of tin and tin-coated metals are widely used because of their corrosion resistance in contact with practically neutral liquids such as water, milk and certain canned foods. Such corrosion as does occur takes the form of localised " black spots " which have been studied by Brennert, whose findings were published by the International Tin Research and Development Council some time ago. (Tech. Pub. Series D., No. 2). Further work on these spots has since been carried out by T. P. Hoar, and is now issued (Tech. Pub., Series A., No. 63). The influence of the surface condition of the tin and the concentration of chloride ion on black-spot formation have been investigated, and a detailed mechanism for the process is proposed. The attack by nearly neutral solutions containing numerous different anions and cations has been studied; the results support and extend the suggested mechanism, and may have value in themselves in exemplifying the corrosion of tin under very various conditions.

A third recent technical publication (Series A, No. 64) of the International Tin Research and Development Council deals with the surface of tinplate. It is stated that during the manufacture of tinplate there is a short period when molten tin and grease films are draining off the sheet. This period is too short for any large change in the distribution of the tin to occur, but there are local effects which are responsible for the production of normal and potential pores. By applying surface tension and viscosity theory to the problem, Dr. Bruce Chalmers has now provided an explanation of the processes of pore formation. When for any reason there is a small non-reactive spot on the steel sheet the layer of molten tin tends to bridge it, but when the spot is over a certain size the film

of tin breaks and forms a pore. Theoretical considerations show that unless the diameter of the non-reactive spot is greater than 0.6 of the local thickness of the tin coating a normal pore cannot be formed. Potential pores are formed when the drops of grease collecting from grease lines during the drawing of the sheet form cups in the tin coating sufficiently deep to expose the tin-iron compound beneath.

Two new instruments have been devised recently for measuring the thickness of tin coating on tinplate. Previous methods of estimation were chemical and suffered from the disadvantage that a considerable time was required, and as the coating had to be removed the tinplate was spoilt. One of the new instruments (Tech. Pub., Series A, No. 66) is magnetic and the other electro-magnetic. They are both capable of giving results rapidly without detriment to the tin coating.

The method of Chalmers and Hoare employs a cobalt chrome-steel permanent magnet and measures the force necessary to pull it off the sheet using a syphon-operated water balance for this purpose. The second instrument, devised by Tait, uses a small transformer which is placed upon the sheet so that the magnetic circuit is the core of the exploring head, the gaps formed by the non-magnetic coating and the basis material. The former is particularly useful for plotting the contour of the surface, and the latter is primarily a workshop instrument for measuring the average thickness and large scale variations.

Some Recent Metallurgical Patents

Coating with Metals

Aluminium and aluminium alloys to be electroplated, particularly with nickel and chromium, are prepared by treating them at a temperature of above 80° C., preferably from 92 to 95° C., with a solution containing hydrochloric acid and ferrous chloride, the content of ferrous chloride tetrahydrate in grams being at least half the content of concentrated hydrochloric acid in cubic centimetres. The contents are preferably approximately equal, for example 40-60 gms. of ferrous chloride tetrahydrate and 40-60 cc. of concentrated hydrochloric acid per litre. The treatment results in a coherent iron coating on the aluminium, etc. See Specification 465,078, of Finckh, Ges., Dr.

Distilling Magnesium

In the continuous production of metallic magnesium by the thermal reduction of magnesiferous raw materials, such as dolomite, with the aid of silicon or ferrosilicon at temperatures substantially below the melting point of the reaction residue, followed by condensation of the magnesium vapour, up to 5 per cent. of an alkaline or alkaline-earth fluoride or mixture of two or more of such compounds are added to the reaction mixture. The fluoride, etc., may be added in the form of dry salts or a solution, the mixture in the latter case being preferably briquetted and the solvent removed, preferably as completely as possible, by drying. See Specification 465,097, of I. G. Farbenindustrie.

Sintered Hard Metal Alloys

A sintered hard metal alloy consists of 0.5-20 per cent. of auxiliary metal, 3-30 per cent. of titanium carbide, 0.3-10 per cent. of vanadium carbide, and the remainder tungsten carbide, each of the three carbides being present in the mixture to be sintered mainly or wholly in free form, and there being more titanium carbide than vanadium carbide. The auxiliary metal may be any one or more of the metals cobalt, nickel, iron, and manganese, or alloys of these with tungsten, molybdenum, or chromium. See Specification 465,323, of Krupp Akt.-Ges., F.

Magnesium from Magnesium Nitride

Magnesium is obtained by heating magnesium nitride to a temperature, for example about 1,600° C., sufficiently high to decompose it into magnesium and nitrogen, in the presence of a substance, which may be a calcium compound such as calcium carbide or silicide, which combines with the nitrogen and prevents its recombination with magnesium. Fluxes such as fluorides may be present. The magnesium may be distilled off at normal or reduced pressure in a current of inert gas, or alternatively in a large excess of hydrogen, and may be collected *in vacuo* or in an inert gas, or it may be combined directly with other metals such as aluminium or beryllium to form alloys. The magnesium nitride may be made by passing nitrogen through a heated mixture of a carbonaceous reducing agent and a magnesium compound such as magnesium oxide. See Specification 464,812, of D. Gardner.

Magnesium Extraction

Magnesium is reduced from its oxide or oxychloride by means of calcium carbide at the time of the production of the carbide or while the carbide is still at a very high temperature from its production, the reduction being effected in a reducing or inert atmosphere and in the absence of moisture, nitrogen, and oxygen, and in some cases under reduced pressure. The resulting slag may be removed in dry form, or a liquid slag may be obtained by the addition of fluxes such as magnesium or aluminium fluoride. The magnesium vapours may be condensed to metal, or alloys may be obtained directly by condensing the vapour in contact with other molten metal. See Specification 464,519, of D. Gardner.

Refining Lead Alloys

Impure lead and lead alloys are treated in the molten condition with sodium and zinc or an alloy or alloys thereof to extract any or all of copper, antimony and arsenic. Alternatively, copper with or without antimony and arsenic is extracted from impure lead or lead alloys containing zinc by treatment with sodium. The latter method is particularly suitable for the treatment of lead which has been desilvered by the Parkes process. Residual sodium may be removed by treatment with steam. Lead-tin alloys may be treated. See Specification 465,346, of Soc. Miniere and Metallurgique de Penarroya.

Ferro-Nickel Alloys

Ferro-nickel is produced by the reduction of ores or metallurgical products containing nickel and iron, the ferro-nickel being then enriched with nickel by blowing in a converter, the blowing being carried out in two or more stages in the first of which enrichment is carried only so far that the slag obtained contains not more than 0.8 per cent. of nickel. The slags obtained in subsequent stages may be re-supplied to the reducing process. The resulting alloy may be refined in a reverberatory or electro furnace to remove sulphur and arsenic and may be used in the production of nickel steel or may be cast into anodes and worked up to pure nickel by electrolysis. See Specification 465,591, of Krupp Gruson-Werk Akt.-Ges., F.

Magnesium Extraction

A process for reducing magnesium from its compounds, including oxides, ores, sulphates, and chlorides, comprises mixing the powdered compound and powdered calcium carbide with a viscous carbonaceous binder such as tar or other hydrocarbon product, and heating the mixture in a reducing or inert atmosphere and in the absence of moisture, nitrogen, and oxygen, and in some cases under reduced pressure, to distil off the magnesium. The resulting slag may be removed in dry form, or a liquid slag may be obtained by the addition of fluxes such as magnesium or aluminium fluoride. The magnesium vapours may be condensed to metal, or alloys may be obtained directly by condensing the vapour in contact with other molten metal. See Specification 464,520, of D. Gardner.

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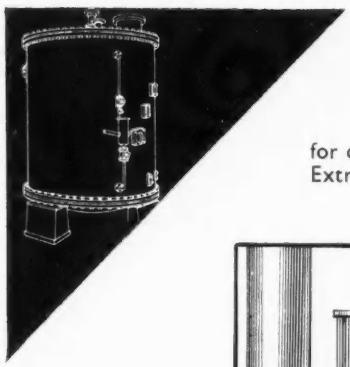

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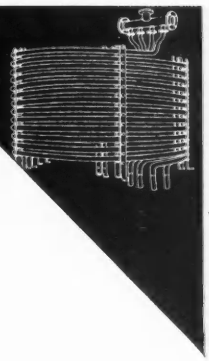

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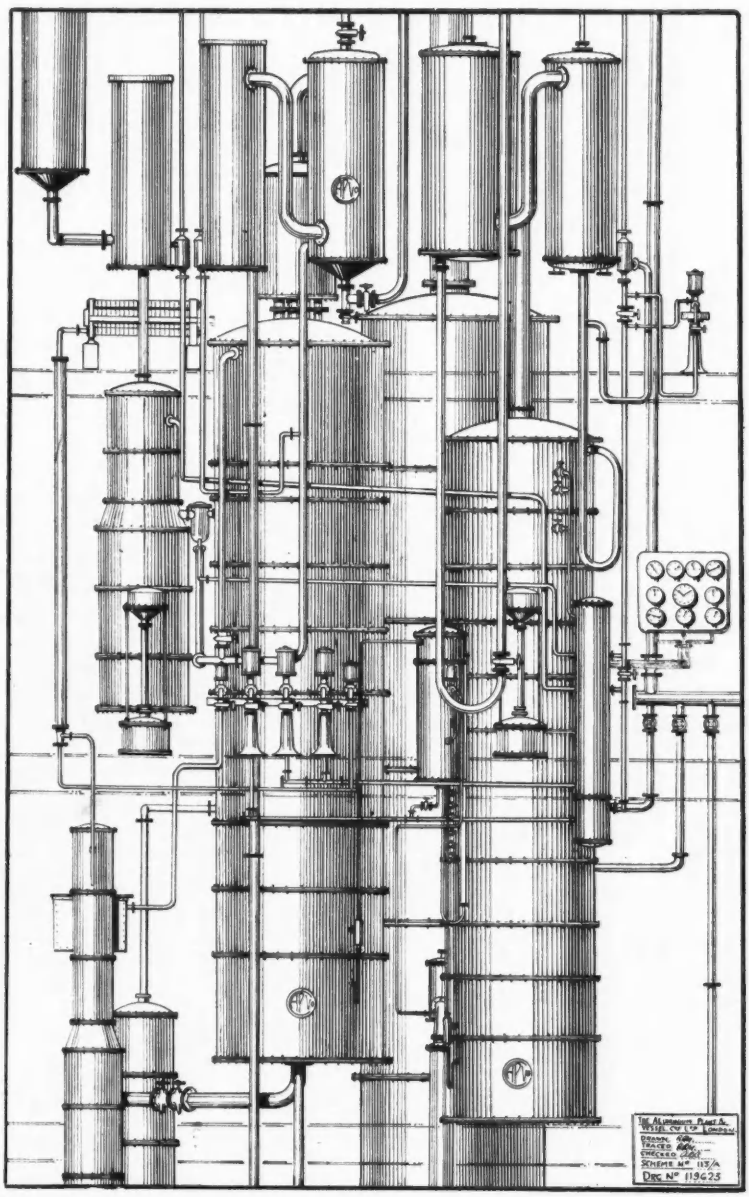

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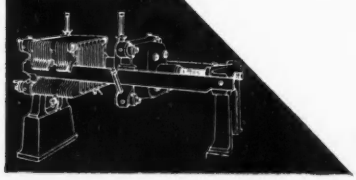

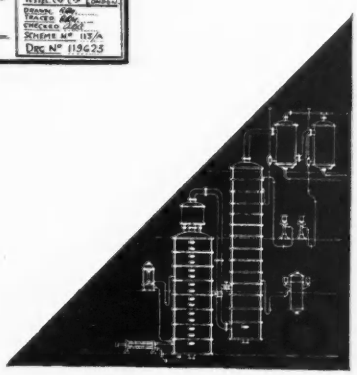

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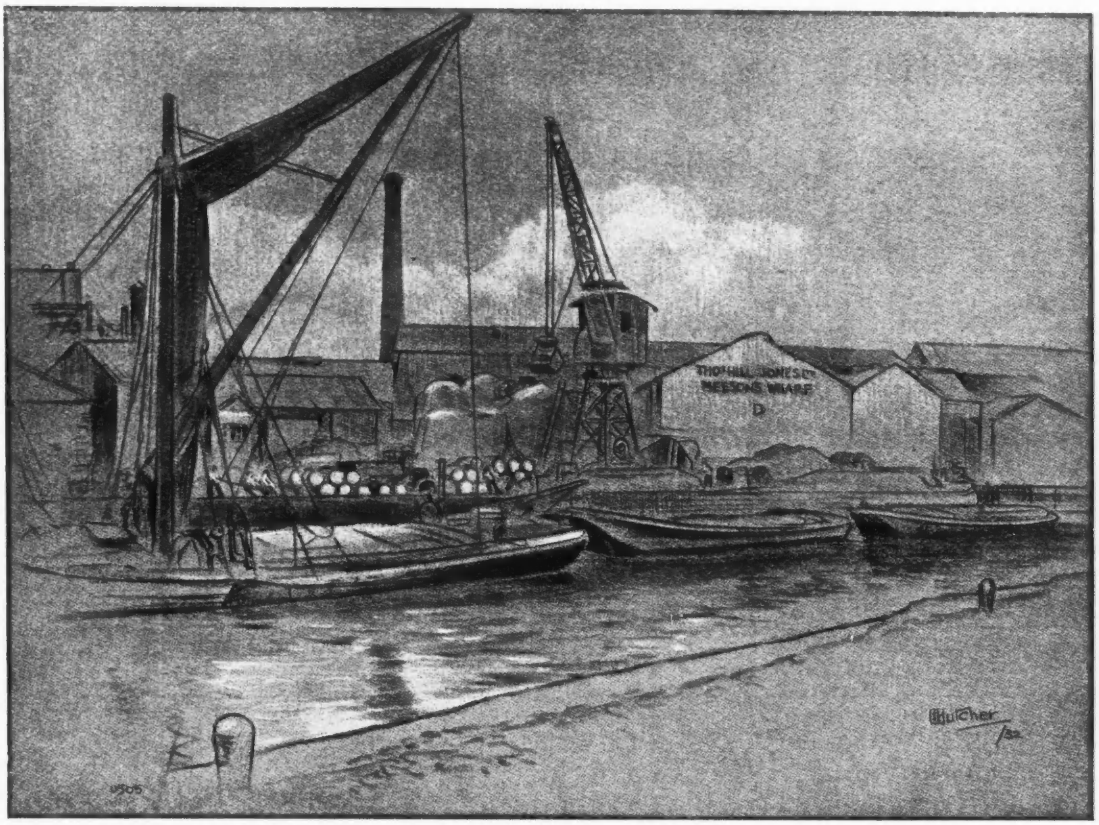

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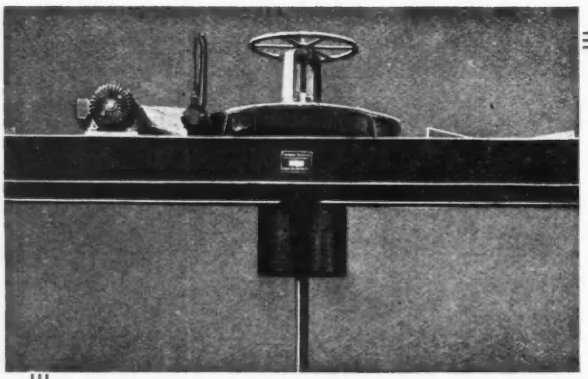

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The Chemical Age

A Weekly Journal Devoted to Industrial and Engineering Chemistry

Vol. XXXVII No. 965 Published every Saturday December 25, 1937

CONTENTS

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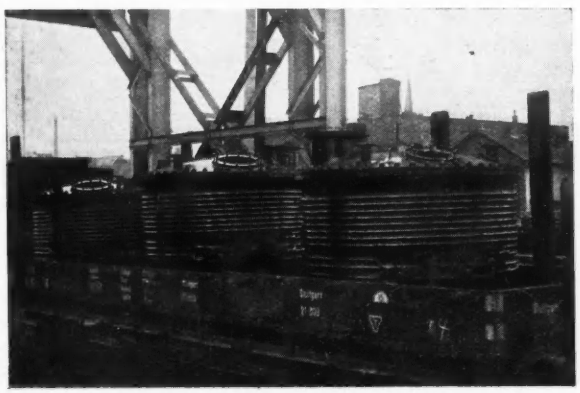

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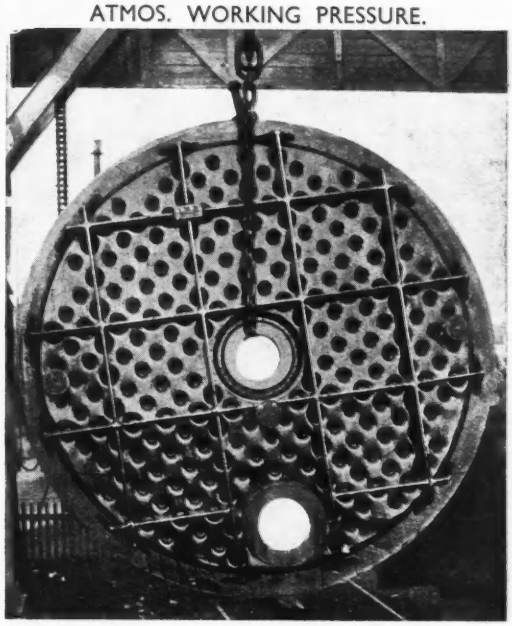

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